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July, 1944

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of the
AMERICAN CHEMICAL SOCIETY

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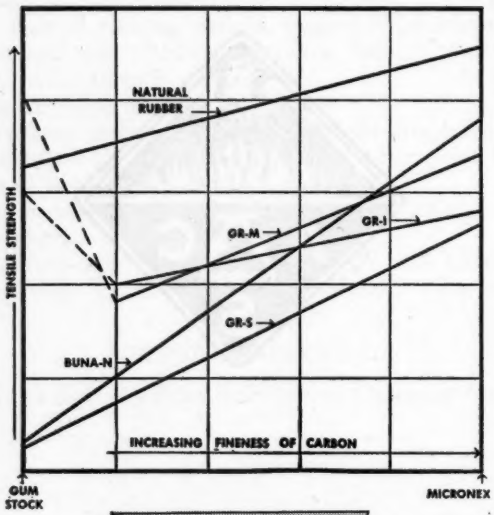

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

SYNTHETIC RESINS AND RUBBERS. By Paul O. Powers, Chief, Organic Research, Armstrong Cork Company. John Wiley & Sons, Inc., New York, N. Y., 1943. v + 296 pp. 49 figs. 13.5 x 21.5 cm. Price, $3.00.—This little book gives a clear and interesting account of the chemistry of more important synthetic resins and rubbers. It opens with a general historical and statistical introduction, including a table listing the names, structural formulas, physical properties and sources of the raw materials from which the industrially important resins are derived. The next chapter discusses the mechanism and kinetics of polymerization and the distinction between linear and cross-linked polymers, and the behavior of catalysts and inhibitors of polymerization. This is followed by separate chapters describing the more important classes of resins now in use industrially. Trade names are avoided throughout. Finally there is a very brief summary of solvents and plasticizers, of the technique of moulding, and the use of resins in formulating protective coatings. Each chapter is followed by review questions and a few additional references, but there is no attempt to cite a literature reference in support of every statement in the text. This book does not compete with the larger books available in completeness, in detail and in giving numerous references. It does not give enough numerical data as to properties of the commercially available resins to be of much help to anyone trying to choose the best resin for a particular application. However, this book can be recommended to a chemist who has not specialized in the field but wishes a readable and reliable general introduction to synthetic resins and synthetic rubbers. [GRINNELL JONES in the *Journal of the American Chemical Society*.]

INDUSTRIAL CHEMISTRY OF COLLOIDAL AND AMORPHOUS MATERIALS. By Warren K. Lewis, Professor in the Department of Chemical Engineering, Massachusetts Institute of Technology, Lombard Squires, Chemical Engineer with E. I. du Pont de Nemours Company, Wilmington, Delaware, and Geoffrey Broughton, Chemical Engineer with the Eastman Kodak Company, Rochester,

N. Y. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1942. xi + 540 pp. Illustrated. 16 x 24 cm. Price, $5.50.—The authors of this very interesting and well-written manual set out to write a text on the industrial chemistry of colloidal and amorphous materials. These they list as emulsions and foams, thermoplastics, glass, paper, plastic fibers, leather, rubber, clays, synthetic resins and plastics, and textile fibers. The technology of each of these materials is clearly and briefly discussed, together with the scientific interpretation of each process and product. For example, x-ray diagrams and other physical chemical data are correlated with industrial procedures. This provides a very interesting and clarified conspectus such as is hardly to be found elsewhere. To lay a foundation for this treatment, the authors devote the first half of the book to a review of physics and of colloid science, beginning with the structure of liquids, and proceeding through viscosity, surface tension, orientation, adsorption, suspensoids, amorphous solids, emulsoids, electrochemical behavior of colloids, gelation, to plastic distortion and flow. The treatment as well as the choice of the data is orthodox, and in accordance with the earlier development of the subject. For example, there is no mention of the essential stabilizing agent in the whole chapter on suspensoids, whereas a stabilizing agent is as necessary here as it is in the formation of emulsions or foams. On the other hand, the authors have rationalized for themselves the subject matter they discuss, and this is done so clearly that the reader is shown the facts as well as the way in which the authors interpret them. The explanations are reasonable and appeal to the engineering mind. The reader is invited by the authors to formulate his own opinions. The authors state—"In a specific problem knowledge of the facts is often inadequate and occasionally in dispute, while understanding of underlying causes is limited and uncertain. Experts disagree on the explanations of phenomena of fundamental importance. In such a situation the scientist tends to withhold judgment, but the technologist is faced with the necessity of making decisions and taking action. Many individuals prefer a purely empirical approach, but it is the conviction of the writers that it is best to submit each problem to a careful, theoretical analysis, even though in the nature of the specific case this may be known to be inadequate. A major purpose, therefore, is the introduction of the student to such a method of attack." To assist in this purpose they supply numerous cross-references, and append a bibliography to each chapter. The book has stood the test of time, embodying the results of twenty-five years' teaching of the subject at the Massachusetts Institute of Technology. The preparation of the manuscript was begun over a dozen years ago by P. K. Frolich, and it has been constantly revised because of the very rapid developments in most of the fields discussed. This admirable book is not only an excellent text but is a unique contribution to the advancement of science and industry. [JAMES W. MCBAIN in the *Journal of the American Chemical Society*.]

THE CHEMISTRY OF SYNTHETIC SUBSTANCES. By Emil Dreher. Translated by Marion Lee Taylor. Published by the Philosophical Library, Inc., 15 East 40th St., New York, N. Y. 5½ x 8¼ in. 103 pp. $3.00.—This book represents a series of previously published essays or articles on the chemistry of macromolecular organic compounds, which existing literature treats chiefly from the standpoint of technical applications. It might also be termed a survey of the principal questions of macromolecular chemistry, and serves as an introduction to acquaintance with the chemical processes which take place in the production of synthetic substances. The scope of the book

is best indicated by the titles of the nine essays, which are as follows: (1) High-Molecular Organic Compounds; (2) Survey of Relations of Synthetic High-Molecular Compounds to Drying Oils; (3) Principles of the Processes of Polymerization; (4) Development of the Chemistry of High-Molecular Organic Compounds; (5) Various Types of Polymerization Products; (6) Influence of the Constitution on the Capacity for Polymerization of Low-Molecular Compounds; (7) The Influence of Substituents on the Capacity for Polymerization of Low-Molecular Compounds; (8) Principles of the Processes of Polycondensation; (9) On the Cognizance of Solubility of High-Molecular Film-Forming Substances. [From *The Rubber Age* of New York.]

THE PROBLEM OF THE ELASTICITY OF RUBBER AND OF RUBBER-LIKE MATERIALS. By Eugene Guth. Department of Physics, University of Notre Dame, Notre Dame, Ind. 7½ x 10¼ in. 25 pp.—Reprinted from Publication No. 21 of the American Association for the Advancement of Science, this report is restricted to the problem of the elasticity of rubber and its solution by some of the new experimental and theoretical investigations. A short discussion of inorganic, organic and biologic rubberlike materials reveals the general occurrence of rubberlike elasticity. Surface films of some high-polymeric substances exhibit reversible elasticity and have a network structure closely resembling that of rubber. In short, this work represents a quantitative solution of the problem of the elasticity of rubber and of rubberlike materials. [From *The Rubber Age* of New York.]

COMPOUNDING MANUAL FOR CHEMIGUM N-1. Goodyear Tire & Rubber Co., Akron 16, Ohio. 9 x 11½ in. 16 pp.—As indicated by the title, this is a compounding manual for Chemigum M-1, the oil-resistant type of synthetic rubber developed by Goodyear. It covers general properties of the material, compounding suggestions, antioxidants, milling, calendering and fabrication, and typical compounds, the latter including moulding, hard packing and extrusion compounds. The manufacture of Chemigum N-1 is also discussed. Other sections in the manual are devoted to important dates in the development of synthetic rubber and the story of Goodyear and synthetic rubber. [From *The Rubber Age* of New York.]

PERBUNAN COMPOUNDING AND PROCESSING MANUAL. Tentative Supplement No. II. Section No. IX. Stanco Distributors, Inc., 26 Broadway, New York, N. Y. 9 pages.—This tentative supplement is being issued to present suggested Perbunan formulations for some applications in accordance with the S.A.E. aeronautical material specifications as revised October 1, 1943. All data presented are based on laboratory methods as recommended by the A.S.T.M. It is pointed out that no suggested compound or series of compounds can be universally applicable to all methods of processing, preparation, or forming, and it is stated that the formulations shown were designed with the idea that they could be readily adapted, but are not presented as universal "cure-alls". Formulas and test data for hydraulic fluid (petroleum base) resistant, low-temperature resistant, extreme-pressure lubricant resistant, and coolant resistant compounds are given. [From the *India Rubber World*.]

THIOKOL TYPE FA—BUNA-S BLENDS. Technical Service Bulletin No. 19. Thiokol Corp., Trenton, N. J. 7 pages.—Stating that Thiokol Type FA may be blended with GR-S in all proportions to effect modifications of vulcanized

and unvulcanized characteristics, this bulletin presents data on such mixtures to assist the compounder in attaining such specific properties as he may require. In blending it is recommended that the Thiokol and the GR-S batches be mixed separately and then blended to obtain the desired polymer ratio. Any fillers ordinarily used in rubber compounding may be used in either or both phases of the blend, and the choice of the accelerators used in the GR-S phase is limited somewhat by consideration of the effect of the accelerators on the Thiokol Type FA, it is stated. Other items covered are the variation in physical properties of tensile, abrasion resistance and elongation, and the effect of blending on solvent and oil resistance, tear resistance, etc. Base formulas for low-loaded and high-loaded GR-S stocks and their use in various combinations with a Thiokol Type FA stock containing 60 parts of SRF black are given. [From the *India Rubber World.*]

NEOPRENE (GR-M). Safeguarding Workers Handling Synthetic Rubber in the Rubber Industry. Rubber Series No. 1. Division of Labor Standards, United States Department of Labor. United States Government Printing Office, Washington 25, D. C. 1944. 48 pages. 10¢.—Prefaced by a brief survey of the Government's rubber program, this bulletin describes the production of GR-M, and discusses fundamental requirements for the conservation of the health of workers in the industry. The survey indicates that no new hazards are involved in processing GR-M. Few materials unfamiliar to the natural rubber industry are involved, and these are receiving intensive study. A chapter dealing with the engineering control of vapors discusses general ventilation and describes special applications for localized exhaust. [From the *India Rubber World.*]

A. S. T. M. STANDARDS ON RUBBER PRODUCTS (WITH RELATED INFORMATION). Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia 2, Pa. February, 1944. Paper, 9 x 6 inches, 424 pages. Price $1.75.—Tentative specifications for rubber and synthetic rubber compounds for automotive and aeronautical applications prepared by Technical Committee A on Automotive Rubber is an important addition to the latest volume of standards prepared by the A. S. T. M. Committee D-11 on Rubber Products. Also included for the first time are specifications for rubber and synthetic-rubber insulation for wire and cable; methods of testing rubber-coated fabrics and asbestos sheet packing; new methods of specifications and tests for nonrigid plastics; and three electrical test methods applicable to rubber products. In addition to 24 general methods are several specifications and methods for rubber hose and belting; rubber gloves, matting, and tape; and latex, rubber cements, sponge and hard rubber products. Several proposed specifications, which have not been formally approved by the Society, are included in draft form for the purpose of soliciting comment. Emergency alternate provisions applying to some standards have been printed on colored paper and bound into the volume in their proper places. [From the *India Rubber World.*]

WEAR. By D. Landau. Nitralloy Corp., 230 Park Ave., New York, N. Y. 6 x 9 in. 46 pp.—Subtitled "A Discussion of the Mechanism of Wear Phenomena and Influencing Factors", this is believed to be the first booklet in English published on the subject of wear. It treats with such angles as the mechanism of wear, wear and physical properties, molecular adhesion, surface melting, specific pressures, lubricants and wear, scoring, fretting, gear pitting, work

hardening, chemical effects and surface finish and wear. The wear of Nitralloy *versus* other steels is also discussed. A comprehensive bibliography on the general subject of wear is included. [From *The Rubber Age* of New York.]

CHEMICAL ENGINEERING CATALOG. 1943–44. Twenty-eighth Annual Edition. Published by the Reinhold Publishing Corp., New York. Cloth, 11¼ x 8½ inches, 1513 pages. Indexed.—Concise and accurate data on equipment, machinery, laboratory supplies, heavy and fine chemicals, and raw materials used by the chemical and related industries, including rubber, have been provided by about 550 firms for the current issue of this standard reference work. The technical data section includes a new humidity chart and various other charts, tables, and monographs, some now out of print, others never previously publicly published. The book section, with brief descriptions of more than 2,500 books in English, has been brought up to date and constitutes a comprehensive bibliography of chemical technology. [From the *India Rubber World.*]

PLASTIC HORIZONS. By B. H. Weil and Victor J. Anhorn. Published by the Jaques Cattell Press, Lancaster, Penna. 5½ x 7½ in. 169 pp. $2.50.—This is an interesting book on the development, current use and probable application of plastics in the future. It is a comprehensive, general book, sufficiently nontechnical for the general public, yet detailed enough to be informative. Without emphasizing details of chemistry, the authors, both associated with the Gulf Research and Development Co., have pointed out scientific relationships and have blended science with economics in an interesting manner. The development of plastics is stressed throughout the book. The authors have not overlooked synthetic rubbers, and it is evident from the 12 pages devoted to this subject that they have carefully diagnosed the past, present and possible future of these rubbers. As in the case of the direct plastics, the history of the various synthetic rubbers—Buna-S, Buna-N, Neoprene, Thiokol, Butyl—is reviewed with specific properties and applications stressed. Some mention is also made of numerous rubberlike materials, including Koroseal, the vinyls, Vistanex, Ethyl rubber, Agripol and Kempol. The section devoted to synthetic rubbers may aptly be termed a concise review of the current situation. The book consists of five chapters in all, as follows: (1) What Are Plastics; (2) Plastics and Our Modern World; (3) Plastics in a World at War; (4) Synthetic Fibers and Synthetic Rubbers; (5) Plastics and the Future. Each chapter is broken down into numerous subsections. In addition, the book contains a section devoted to names, chemical types, and manufacturers of familiar plastics and related materials. Asterisks are employed to indicate the specific uses of many of the plastics listed. A cross-referenced subject index is included. [From *The Rubber Age* of New York.]

THE CHEMICAL FORMULARY. Volume VI. H. Bennett, Editor-in-Chief. Published by the Chemical Publishing Co., Brooklyn, N. Y. 1943. Cloth, 8½ x 5½ inches, 636 pages. Index. Price $6.00.—This collection of practical formulas for making thousands of products in the rubber, resins, plastics, adhesives, emulsions, and about 15 other industries offers tested recipes ranging from artificial rubber latex to a zinc coating for iron. Some of the formulas have been used commercially; others have been obtained from patent literature, a source less valuable because of errors and omissions. Because many chemical products, however, are not definite chemical compounds, but mixtures or com-

plex blends, the formulary fills a current need of a modern compilation. The literature in the past has been scattered, meager, and outmoded. The volume will save chemists and allied workers time and effort. Rubber formulas include recipes for rubber preservatives, eraser rubber, leatherlike stiff rubber, synthetic-rubber gear composition, golf-ball cover composition, Neoprene gasket and packing (British patent), Thiokol printing roller, and a method of reclaiming rubber. Butyl compounds for wire insulation and moulded good, three Buna-S compounds, and German patents for Buna-N and Buna-S are given. A list of substitutes or alternatives for about 300 scarce chemicals and products may be of assistance to many users of the volume. Several time-saving tables and a long list of materials and their suppliers add utility to the encyclopedia. [From the *India Rubber World.*]

CLASSIFIED DIRECTORY of Consulting Chemists and Chemical Engineers. Eighth Edition. 1944. Association of Consulting Chemists & Chemical Engineers, Inc., 50 E. 41st St., New York. 96 pages.—This latest, revised, and enlarged eighth edition of the "Classified Directory of Consulting Chemists and Chemical Engineers" lists in Section I the key sheet in which fields covered by the various consultants, such as acids, catalysis, colloids, rubber, metals, organic research, plastics, etc., are given, and the members or firms specializing or qualified to work in the different fields are indicated by their key numbers. An index of page and key numbers, which have been made identical for easy reference precedes the main key sheet. Detailed scope sheets giving qualifications of the many consultant firms, their scope, and activities comprise the main portion of the directory. A membership list in alphabetical order and also according to geographical location is included, and excerpts from the code of ethics and the by-laws of the Association are found on the inside front and back covers of the directory. [From the *India Rubber World.*]

WARTIME PRICES. Part 1. August 1939 to Pearl Harbor. John M. Blair and Melville J. Ulmer under the direction of Saul Nelson. Bulletin 749. United States Department of Labor, Bureau of Labor Statistics. U. S. Government Printing Office, Washington, D. C. 1944. 272 pages. 35¢.—This general review of price movements in the United States from the invasion of Poland to the attack on Pearl Harbor is mainly based on price data collected by the Wholesale Price Division of the Bureau of Labor Statistics. It covers foods, textiles, fuels, metals, paper, chemicals, rubber, and other commodities. The short summary on crude rubber presents the various factors responsible for the fluctuations in prices, stocks, imports, and consumption during the tense period of defense activity. [From the *India Rubber World.*]

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, NEW YORK, N. Y.

APRIL 26, 27 AND 28, 1944

The Division of Rubber Chemistry convened in New York City for its April, 1944, meeting. For the second consecutive time the Division was forced to meet separately from the American Chemical Society because of the

limited housing facilities in Cleveland, Ohio, where the Society met earlier in the same month. The headquarters of the Division were again at the Commodore Hotel.

The meeting was under the chairmanship of Harold Gray, and the local arrangements were under the direction of H. E. Outcault and his committee of W. J. Geldard, S. Collier, J. Breckley, E. S. Kern, P. P. Pinto, F. S. Conover, R. G. Seaman, M. F. Davis, I. E. Lightbown, and B. B. Wilson.

The attendance at the meeting set another record, with total registration of 1225. The following papers were presented:

1. Introduction. Harold Gray.
2. Preparation and Properties of Vulcanized Acrylic Resins, Copolymers of Ethyl Acrylate, and Allyl Maleate. W. C. Mast, Lee T. Smith and C. H. Fisher.
3. Lactoprene: A New Synthetic Rubber: Preparation and Properties of Vulcanized Acrylic Resins. C. H. Fisher, W. C. Mast, C. E. Rehberg and Lee T. Smith.
4. Electron-Microscope Studies of Natural and Synthetic-Rubber Fibers. C. E. Hall, E. A. Hauser, D. S. leBeau, F. O. Schmitt and P. Talalay.
5. Effect of Milling on the Properties of Hevea and Buna Rubbers. W. B. Wiegand and H. A. Braendle.
6. Structural Features of Buna-S (GR-S) in Relation to Physical Properties. A. R. Kemp and W. G. Straitiff.
7. A GR-S Vulcanization Catalyst. A. A. Somerville.
8. Heat Aging of GR-S Stocks. G. M. Massie.
9. Effect of Atmospheric Humidity during Storage of Uncured Stock on Stress-Strain Characteristics and Rate of Cure in Testing of GR-S. F. E. Rupert and F. W. Gage.
10. Effect of Moisture on the Curing Rate of GR-S. W. B. Wiegand and H. A. Braendle.
11. A Basic Compounding Study of Carbon and Noncarbon Pigments on GR-S. Alan R. Lukens.
12. The Reënforcement of GR-S with Zinc Oxide. H. C. Jones.
13. Pigment Incorporation in GR-S through Latex. W. McMahon and A. R. Kemp.
14. Some Factors Influencing the Processability of GR-S. A. M. Neal and P. Ottenhoff.
15. Alkyl Phenol Sulfides as a Class of Vulcanizing Agents. G. M. Wolf, T. E. Deger, H. I. Cramer and C. C. deHilster.
16. Vulcanization of GR-I. F. P. Baldwin, R. L. Zapp and L. B. Turner.
17. An Improved Method for the Control of the pH of Neoprene Latex. H. K. Livingston and R. H. Walsh.
18. Mixture of Acrylonitrile-Butadiene Copolymers with Plasticized Polyvinyl Chloride. R. A. Emmett.
19. Vinyl Butyrals in the Rubber Industry. D. S. Plumb.
20. A Method for Predicting the Volume Increase of Perbunan Compounds in Petroleum Products. R. M. Howlett.
21. Swelling of Synthetic Rubbers in Mineral Oils: Effect of Temperature and of Aniline Point. P. O. Powers and B. R. Billmeyer.
22. Determination of Rate of Cure, GR-I and Natural Rubber. Leonard H. Cohan, Madeline Sohn and Martin Steinberg.
23. Vulcanization of Buna-S and Rubber. La Verne E. Cheyney.

24. The Chemistry of Sulfur Vulcanization. Robert T. Armstrong, Julian R. Little and Kenneth W. Doak.
25. Electrical Conductivity of Carbon Black Loaded Rubber Stocks. G. Goldfinger and W. R. Smith.
26. Theory of the Stiffening Effect of Pigments in Rubber. S. D. Gehman.
27. The Processing Behavior of High Polymers as Revealed by Their Elastic-Plastic Properties. R. L. Zapp and A. M. Gessler.
28. The Identification of Natural and Synthetic Rubbers. H. P. Burchfield.
29. A Simplified Hot Tensile Test for GR-S. W. B. Wiegand and H. A. Braendle.
30. Aging of GR-S Type Vulcanizates in Air, Oxygen and Nitrogen. J. Reid Shelton and Hugh Winn.
31. Time-Temperature Relationships in the Oven-Aging of GR-S. Staunton R. Harrison and Otis D. Cole.
32. The Effects of Elastomer Crystallization on Tests for Freeze Resistance. D. B. Forman.
33. The Use of an A. C. Solenoid in Freeze Tests. H. G. Bimmerman and W. N. Keen.

The Divisional banquet was held in the main ballroom of the Commodore on Thursday evening, with 935 present. Dr. C. L. Parsons, Secretary and General Manager of the American Chemical Society, "reminisced" on the formation and early growth of the Division of Rubber Chemistry and on his association with its founders.

The Chairman introduced the following honored guests: C. A. Parsons, V. du Vigneaud, Alden H. Emery, W. J. Murphy, E. B. Babcock, B. J. O'Donnell, A. V. Petrenko, and E. R. Rowzee.

The Officers of the Division and the Chairmen of the local rubber groups met with Secretary Parsons and A. H. Emery to work out a program for the promotion of closer collaboration between the groups and the Division. On this occasion a number of questions growing out of the relationship of the groups to the Division and the Society were harmoniously resolved, and tentative arrangements were agreed upon for the interchange of program information and speakers between the various groups. This function was so well received that plans were made to continue the practice of holding such a "get-together" at future meetings of the Division.

The following nominees, submitted by the Nominating Committee under the chairmanship of H. L. Trumbull, were presented during the business meeting:

Chairman	W. A. Gibbons
Vice-Chairman	A. H. Nellen
	W. W. Vogt
Secretary	H. I. Cramer
Treasurer	C. W. Christensen
Sergeant-at-Arms	D. L. Flanders
	E. H. Nahm
Directors	Fred Amon
	B. S. Garvey
	C. R. Haynes
	W. G. Nelson
	H. J. Osterhof
	R. A. Schatzel

The Chairman of the Membership Committee, C. R. Haynes, reported a continuing increase in the membership of the Division, then 1180 (including full and associate members). An abstract of the report of the Crude Rubber Committee was read by the Secretary. The complete report can be found on pages 529–532 of the April 1944 issue of RUBBER CHEMISTRY AND TECHNOLOGY.

The Chairman announced that a number of changes in policy have been effected by the Executive Committee since the present By-Laws of the Division were adopted in September 1939, and that the present Executive Committee had created a special committee, composed of W. A. Gibbons, H. E. Outcault and the Secretary, to study the present By-Laws and recommend revisions at the next meeting. It was announced that, due to the shortage of paper for the publishing of RUBBER CHEMISTRY AND TECHNOLOGY, the Executive Committee had voted to suspend acceptance of new members, new associate members and new subscriptions until such time as the Editor of RUBBER CHEMISTRY AND TECHNOLOGY is assured of sufficient paper to keep our publication up to its usual high standard.

H. I. CRAMER
Secretary

STRESS RELAXATION OF NATURAL AND SYNTHETIC RUBBER STOCKS *

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The study of the dependence of stress at constant elongation and temperature on time of application appears to hold considerable promise in the evaluation of rubberlike materials. Stress relaxation apparatus is rather simple to construct and the measurements can be made with higher precision than is possible, for example, with the conventional stress-strain test, where rate of strain strongly influences the result.

The series of experiments described in this paper was undertaken to study the nature and the resistance to deterioration of the structures of several synthetic rubbers and natural rubber in vulcanized gum and tread type stocks. The measurements were made over a range of temperatures and elongations. The data for the decay of stress with time, and especially the temperature dependence of these data, indicated very strongly that a definite chemical reaction is involved in the deterioration of these rubber structures. The decay of stress acts as a physical index of this chemical deterioration, and the accuracy with which the phenomena can be explained on the basis of current theories of molecular structure of rubberlike polymers affords a partial confirmation of these structural concepts.

APPARATUS AND METHODS OF MEASUREMENT

The apparatus used in this work consisted essentially of a special beam balance operating against the stress of an elongated band of the rubberlike material. A single unit of the apparatus is shown in Figure 1. The ring sample S [$2^{11}/_{16}$ inches O.D., $2^{5}/_{16}$ inches I.D.] was died out of cured sheet 0.028 inch to 0.054 inch in thickness. It was stretched between two stainless-steel flanged pulleys A and B. The diameter of the pulleys was $^{3}/_{8}$ inch. The upper pulley A was rigidly fastened to the balance arm. The lower pulley B was free to rotate on the bent rod C. The bent rod was drilled axially to fit a horizontal stud mounted on the vertically movable clamp D. The elongation chosen for the test could be varied from 0 to 250 per cent by setting the clamp D in the proper position. Higher elongations could be obtained by use of a ring sample of smaller diameter. The rod C extended through the floor of the constant temperature box so that it could be manipulated from outside. Thus, the samples could be hung over A and allowed to come to the desired temperature; then quickly hooked by the pulley B and brought to the desired elongation by pushing B onto the stud.

The fulcrum of the balance consisted of two stationary agate V-blocks in which rode a hardened steel wedge attached to the beam. The weight E was

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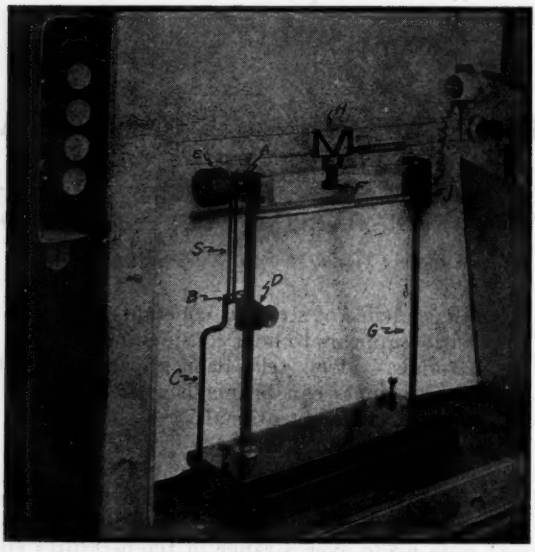

FIG. 1.—Single unit of stress relaxation apparatus.

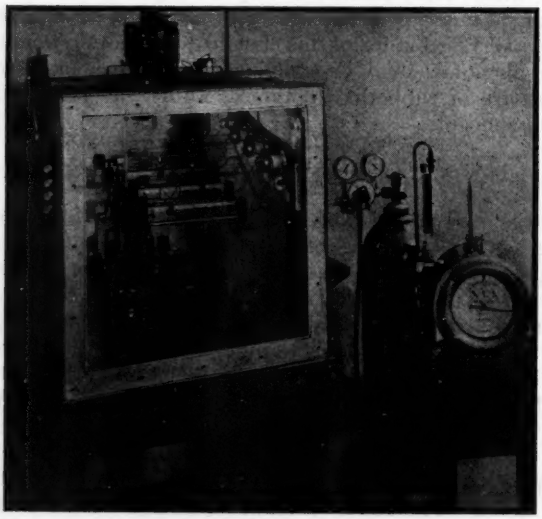

FIG. 2.—General view of stress relaxation apparatus.

adjustable so that the beam could be balanced with the rider weight *F* at the extreme left of the scale. The smallest division on the brass beam was 0.02 pound, but it could be read to within 0.002 pound. Additional weights could be suspended on the wire *G* below the box. The rider weight was manipulated from outside the box by means of the trolley mechanism *H*.

The maximum vertical motion of the extreme right end of the beam was ⅛ inch, which corresponded to an elongation of 0.19 per cent, based on the un-

stretched length of the band. A set of electrical contacts was mounted in the Bakelite member *J* so that the neon bulb lighted when the right end of the beam dropped. A slight flickering of the bulb was taken as an indication of balance against the stress exerted by the band. The initial length of the band was taken as the average circumference of the ring minus the circumference of one pulley.

The whole apparatus assembly with the four balance units is shown in Figure 2, with the triple glass front of the box removed. In some tests, water-pumped nitrogen was passed through the box at a rate of 8 cu. ft. per hour, which assured a reasonably low oxygen concentration in the chamber. The

TABLE I

POLYMERS AND CURES

Compd.	Stock No.	Polymer	Minutes cure at 270° F (132.2° C)
A-G	R198	Hevea smoked sheet	75
A-T	R199	Hevea smoked sheet	75
B-G	R200	Buna-S 85/15* medium conversion	100
B-T	R201	Buna-S 85/15* medium conversion	100
B-G	R202	Buna-S 75/25* medium conversion (GR-S)	100
B-T	R203	Buna-S 75/25* medium conversion (GR-S)	125
B-G	R204	Buna-S 60/40* medium conversion	100
B-T	R205	Buna-S 60/40* medium conversion	100
B-G	R206	Buna-S 75/25* low conversion	75
B-T	R207	Buna-S 75/25* low conversion	100
B-G	R208	Buna-S 72/25* high conversion	100
B-T	R209	Buna-S 75/25* high conversion	100
B-G	R214	Polybutadiene	100
B-T	R215	Polybutadiene	100
C-G	R210	Butaprene-NM	75
C-T	R211	Butaprene-NM	100
C-G	R212	Butaprene-NX	50
C-T	R213	Butaprene-NX	50
C-G	R218	Butaprene-N	75
C-T	R219	Butaprene-N	75
C-G	R226	Butaprene-NM (low fatty acid)	75
C-T	R227	Butaprene-NM (low fatty acid)	100
D-G	R216	Neoprene-GN	100
D-T	R217	Neoprene-GN	100
E-G	R262	Hevea smoked sheet	40
E-T	R261	Hevea smoked sheet	40
F-G	R264	Buna-S 75/25* medium conversion	40
F-T	R263	Buna-S 75/25* medium conversion	40
G-G	R269	Hevea smoked sheet 90 min. at 300° F	—
H-G	R270	Buna-S 75/25* med. conversion 90 min. at 300° F	—
I-G	R278	Buna-S† (no antioxidant) 75/25*	100
I-T	R279	Buna-S† (no antioxidant) 75/25*	125
J-G	R280	Buna-S† (antioxidant added) 75/25*	100
J-T	R281	Buna-S† (antioxidant added) 75/25*	125

* Butadiene/styrene ratio. † Sulfur stabilized.

TABLE II

RECIPES

	A-G	A-T	B-G	B-T	C-G	C-T	D-G	D-T	E-G	E-T	F-G	F-T	G-G	H-G	I-G	I-T	J-G	J-T
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	3	3	2	2	2.5	3	—	—	—	—	—	—	13	13	—	—	—	—
Zinc oxide	3	3	5	5	5	5	5	5	3	3	5	5	3	5	5	5	5	5
Stearic acid	0.5	3.5	0.5	3	1	3	0.5	0.5	0.5	3.5	0.5	3	0.5	0.5	0.5	3	0.5	3
Captax	1	1	1.5	1.5	1.5	1.5	—	—	—	—	—	—	1	1.5	1.5	1.5	1.5	1.5
Agerite Powder	1	1	—	—	—	—	1	1	1	1	—	—	1	—	—	—	—	2
Pine tar	—	3	—	—	—	—	—	—	—	3	—	—	—	—	—	—	—	2
Bardol	—	—	—	5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dibutyl phthalate	—	—	—	—	—	20	—	—	—	—	—	5	—	—	—	5	—	5
Cottonseed oil	—	—	—	—	—	—	2.5	2.5	—	—	—	—	—	—	—	—	—	—
Calcined light magnesia	—	—	—	—	—	—	4	4	—	—	—	—	—	—	—	—	—	—
Altax	—	—	—	—	—	—	0.75	0.75	—	—	—	—	—	—	—	—	—	—
Pip-pip	—	—	—	—	—	—	0.5	0.5	—	—	—	—	—	—	—	—	—	—
Channel black	—	50	—	50	—	50	—	50	—	50	—	50	—	—	—	50	—	50
Paraquinone dioxime	—	—	—	—	—	—	—	—	2	2	2	2	—	—	—	—	—	—
Lead dioxide	—	—	—	—	—	—	—	—	3	3	3	3	—	—	—	—	—	—

box was tightly sealed except for short periods when the holes necessary for free motion of the wires were opened to allow measurements. Samples were placed in a vacuum chamber and degassed at about 0.1 mm. Hg pressure for two hours, with three intervening flushings with nitrogen in an effort to reduce the oxygen content in the outer regions of the bands. They were then placed in the chamber, preheated in the unstrained state for 15 minutes, then extended. Stress readings were possible as early as seven seconds after extension and were continued for 20 to 300 hours, depending on the nature of the samples, the temperature, and the elongation[1].

The experiments were made on vulcanized gum and tread type stocks of five basic kinds: natural rubber, Neoprene, Butyl rubber, Buna-S (butadiene-styrene copolymer)[2], and Butaprene-N (butadiene-acrylonitrile copolymer). The Buna-S polymers were of differing styrene contents and of differing degrees of conversion. The series included GR-S.

Most of the polymers employed are listed in Table I, with the compound numbers and optimum tensile cures. The corresponding compound formulas are given in Table II. Gum stock formulas (no carbon black) were selected

TABLE III

COMPOUND FORMULAS OF BUTYL STOCKS

	B-3 Gum 4007-2	B-3 Low black 3861-4	B-3 High black 3861-5	B-1.45 Gum 4007-1	B-1.45 Low black 3861-1	B-1.45 High black 3861-2
Butyl B-3	100	100	100	—	—	—
Butyl B-1.45	—	—	—	100	100	100
Sulfur	1.5	1.5	2.0	1.5	1.5	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	3.0	3.0	3.0	3.0	3.0	3.0
Captax	—	—	0.5	—	—	0.5
Tuads	1.0	1.0	1.0	1.0	1.0	1.0
Coarse carbon black	—	10.0	50.0	—	10.0	50.0

All cures, 60 minutes at 307° F

with the aim of simplicity and uniformity of formulation for the different polymers. Tread type stocks were compounded with 50 parts by weight of channel black per 100 parts of polymer, and with the minimum addition of softener necessary to give good mixing on the laboratory mill. Mixing methods were selected to give thorough pigment dispersions and minimum mill temperatures.

Some of the polymers were specially compounded[3]. For example, Hevea and GR-S were vulcanized without sulfur (by use of paraquinone dioxime and lead dioxide). A special sulfur-stabilized GR-S polymer was also prepared for comparison with the same material to which antioxidant had been added.

OUTLINE OF EXPERIMENTAL RESULTS

The experimental results are shown in the form of graphs and tables. In the graphs, stress is plotted against logarithmic time for reasons of convenience. The curves were very reproducible, the maximum deviation in stress at a given time in successive experiments on different rubber bands of the same stock being about 4.0 per cent. A result not previously reported in the literature is apparent from these graphs. A complete decay of stress in these rubbers was indicated in a time that became exponentially smaller with increase in

temperature. At 100° C the stress in natural rubber was practically completely decayed in 100 hours independent of the presence of carbon black in the rubber (see Figure 3).

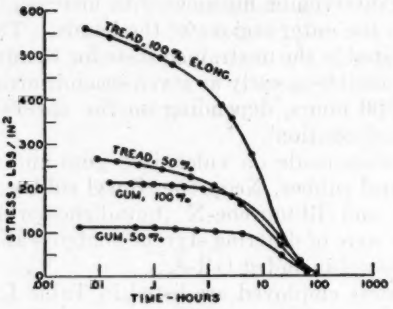

FIG. 3.—Hevea rubber stocks; 100° C.

At lower temperatures, especially when stress is plotted against linear time, the fact that the stress would decay to zero in a sufficiently long time is not apparent. Meyer in his recent book[4] stated that in vulcanized rubber a minimum positive stress value is reached with time. The results of these experiments, however, showed that complete relaxation occurred at temperatures at and above 100° C, and there was no evidence of the existence of a minimum positive stress at temperatures as low as 40° C (see Figures 4 and 5). In

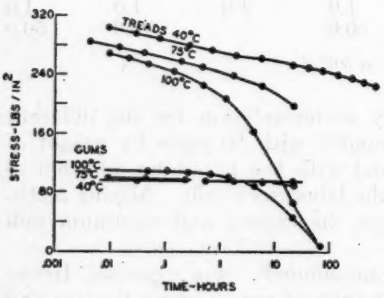

FIG. 4.—Hevea stocks; 50 per cent elongation.

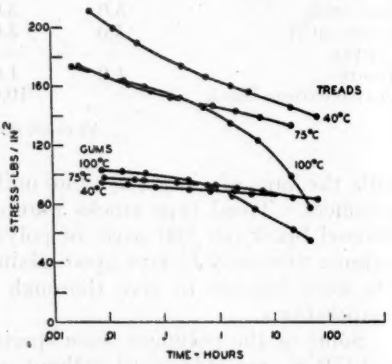

FIG. 5.—Buna-S (GR-S) 75/25 medium conversion; 50 per cent elongation.

view of the close agreement of the temperature dependence of the data at the higher temperatures with that predicted by current chemical rate theories, it was quite possible that complete relaxation would have been observed in extended experiments at the lower temperatures.

Besides the striking fact that the decay of stress became complete at the same time for rubbers without carbon black and for the same rubber containing 50 parts carbon black per 100 parts rubber, it is to be noted as seen in Figures 3, 6, and 7 that variation of the elongation did not greatly change the rate of decay of stress. This is shown even more strikingly in Figures 8 and 9, where

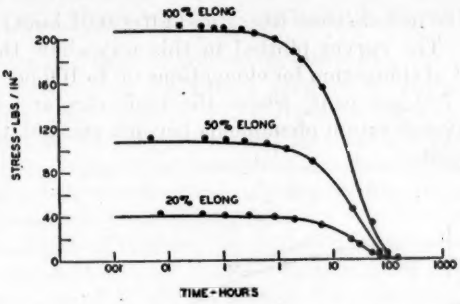

FIG. 6.—Hevea gum stock; 100° C. Experimental points, theoretical curves.

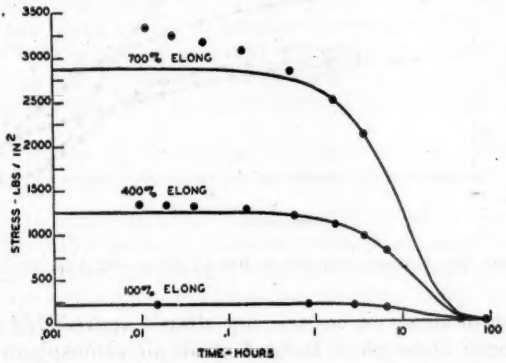

FIG. 7.—Hevea gum stock; 100° C. Experimental points, theoretical curves.

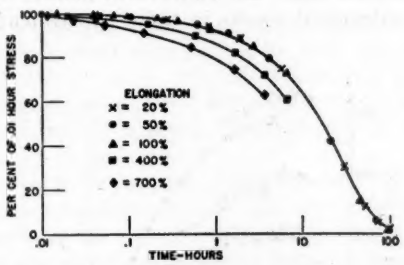

FIG. 8.—Effect of percentage elongation on relaxation rate; Hevea gum, 100° C.

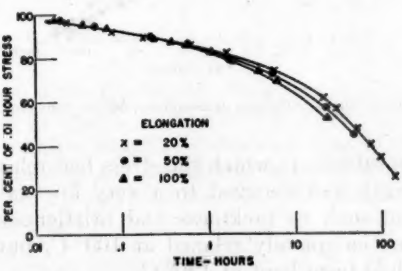

FIG. 9.—Effect of percentage elongation on relaxation rate; GR-S tread, 100° C.

stress divided by the initial stress (measured after 0.01 hour) is plotted against logarithmic time. The curves plotted in this way show that the relaxation rate is independent of elongation for elongations up to 100 per cent. At elongations of 400 and 700 per cent, where the molecules are approaching their elastic limit and crystallization phenomena become marked, the relaxation rate is somewhat hastened.

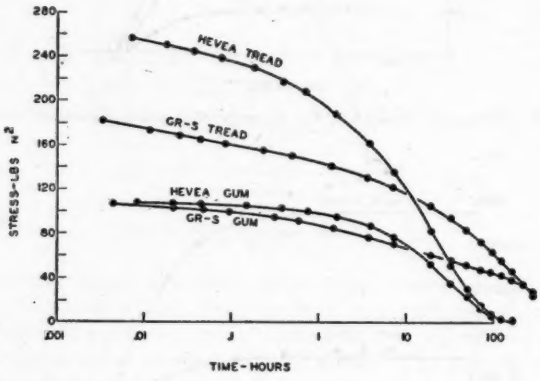

FIG. 10.—Nitrogen atmosphere; 100° C; 50 per cent elongation.

The relaxation of stress curves was not altered appreciably by the use of a commercial nitrogen atmosphere instead of an air atmosphere (compare Figures 10 and 13). Nor did the use of a sulfurless vulcanization (by paraquinone dioxime and lead dioxide) cause the rubbers to behave very differently from the ordinary sulfur vulcanized stocks in these experiments. (See Figure 11.)

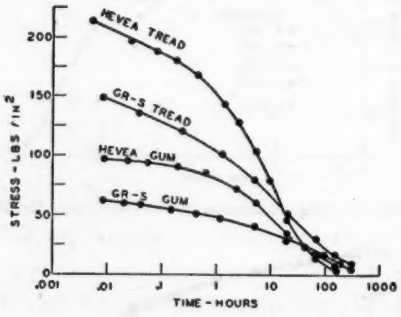

FIG. 11.—Sulfurless stocks; nitrogen atmosphere; 50 per cent elongation; 100° C.

Observation of the rubbers in which the stress had relaxed to zero indicated that the tensile strength had decayed to a very low value. Gross external evidences of oxidation such as tackiness and brittleness were not found in samples that had been completely relaxed at 100° C, but were noticeable in similar samples that had been kept at 120° C.

THEORETICAL DISCUSSION OF DATA

Rubberlike substances may be considered networks composed of long chain molecules. The juncture points of such a network are rather infrequent cross-links between the chains, some of these cross-linking bonds being primary chemical bonds, and others being of a secondary nature, such as dipole-dipole interaction or other strong local interaction between chains. The elastic properties of these substances are probably largely due to the uncoiling of the long molecules between network junctures.

In the case of vulcanized rubbers, the network junctures are probably tetrafunctional in the sense that four chains emanate from each cross bond. If network chains are defined as the portion of the network between successive network junctures then the number of chains between cross-links is twice the number of cross-linking bonds.

When a rubber band is held at constant extension, the stress in the band begins to decay with time. The initial decay is due to relaxing of secondary network junctures. The relatively large decay of stress, which occurs later on, may be interpreted as due to one or both of the following causes.

1. Bond Rupture by Oxidative Scission at Some Point along the Molecular Chains or at the Network Junctures

Inasmuch as the same relaxation curve was obtained in commercial nitrogen as in air and also since no mass oxidation was observable from the physical appearance of the relaxed specimens, only a small amount of oxygen appeared to be necessary for cutting the chains if the complete decay of stress proceeded by this mechanism[5].

2. Spontaneous Bond Rupture at or Adjacent to the Cross-Linking Bonds Put in by Vulcanization

The cross-linking bonds may have quite low energies. In fact, the strength of the peroxide bond has been reported as 34 kcal. per mole and a recently reported value for breaking the S−S bond (when ring sulfur is converted to chain sulfur) was 27.5 kcal. per mole[6]. However, it is to be noted that different vulcanizing agents caused no appreciable difference in the relaxation time. (Compare Figures 3 and 11.)

It is to be realized that the rupture of the network will occur via the easiest route. Thus though mechanisms (1) and (2) are both *a priori* possible, the complete decay of stress in the network will be due to the rupture of the bond, recurring throughout the structure, with the lowest energy.

From the kinetic theory of elasticity[7], the stress is given by:

$$\tau = skT\left[\frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2\right] \tag{1}$$

where τ is the tension, s the number of chains per unit volume supporting the stress, k Boltzmann's constant, T the absolute temperature, and l/l_0 the ratio of stretched to unstretched length. Although Equation (1) is not exact, it shows what is important in the discussion; namely, that the stress is proportional to the number of effective chains per unit volume.

Alternatively, one can write:

$$\tau = (S_1 + S_2)kT\left[\frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2\right] \tag{2}$$

where S_1 is the number of chains per unit volume terminated at both ends by primary cross-bonds and S_2 the number of chains per unit volume terminated by at least one secondary bond.

The relaxation of secondary network bonds plays a role in the initial portion of the experiment at sufficiently low temperatures. These postulated bonds have a natural time of relaxation; that is, the bonds break and remake in new positions which allow the molecular chains to resume coiled configurations and thus release the stress. This phenomenon is distinguished from the breaking of primary bonds by being completely reversible.

In large part, the observable decay of stress at high temperatures is due to the breaking of bonds of the kind postulated in mechanisms (1) and (2) above. These bonds do not remake, and the processes are not reversible, as was seen by the fact that the tensile strength of the rubber bands decayed concomitantly. At fairly high temperature the number of secondary bonds holding the stress has decayed practically to zero in the time before the first measurement is taken. In this case the number of chains per unit volume supporting the stress is reduced by bond rupture somewhere along these chains by the following law:

$$-\frac{1}{S_1}\frac{dS_1}{dt} = K'_{S_1} \tag{3}$$

where K'_{S_1} is a reaction rate constant which by the theory of absolute reaction rates is given by:

$$K'_{S_1} = kT/h \exp\left(-\Delta F_1^{\ddagger}/RT\right) \tag{4}$$

where k is Boltzmann's constant, h is Planck's constant, R the gas constant, $\Delta F_1^{\ddagger}$ the free energy of activation per mole, and T the absolute temperature.

Integration of Equation (3) and substitution in (1) gives:

$$\tau = S_{1,0} \exp\left(-K'_{S_1}t\right)kT\left[\frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2\right] \tag{5}$$

where $S_{1,0}$ is the initial number of chains per unit volume. Otherwise stated:

$$\tau = \tau_0 \exp\left(-K'_{S_1}t\right), \tag{6}$$

where τ_0 is the initial stress. More generally, the expression that should be valid for low temperatures is:

$$\tau = \left(S_{1,0} \exp\left(-K'_{S_1}t\right) + S_{2,0} \exp\left(-K'_{S_2}t\right)\right)kT\left[\frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2\right] \tag{7}$$

Equation (6) agreed remarkably well with the observed relaxation of stress for natural gum rubber (see Figures 6 and 12). The reaction rate constant K_S' turned out to be nearly independent of the elongation of the rubber (and therefore independent of the stress in the network). In the range studied, the temperature dependence of K_S' was given with great exactness by Equation (4), with $\Delta F^{\ddagger}$ being entirely energy of activation (no entropy of activation). $\Delta F^{\ddagger}$ for natural gum rubber turned out to be 30.4 kcal. per mole and the exactness of the temperature relationship of K_S' is shown by Figure 12, which gives theoretical curves and observed data. The theoretical curves were all obtained by assuming $\Delta F^{\ddagger} = 30.4$ kcal. per mole, taking the observed values for τ_0

(with a slight correction of less than three per cent for secondary bond slippage) and determining the curves from Equations (4) and (6).

The independence of $\Delta F^{\ddagger}$ on the elongation is shown in Figures 6–9, where theoretical curves are plotted against observed points for Hevea gum at 100° C and at different elongations. At the very high elongations (400 and 700 per cent) the theoretical equations did not fit the data with the same exactness as

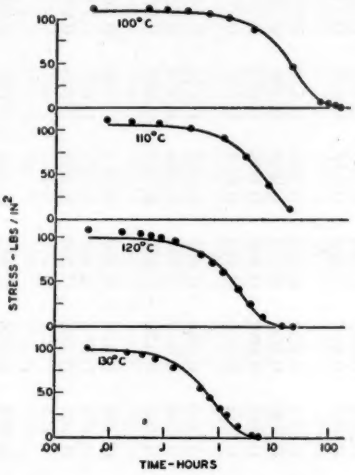

FIG. 12.—Hevea gum stock; 50 per cent elongation. Experimental points, theoretical curves.

at the lower elongations (Figure 7). Also the specimens broke before the decay of stress was very considerable. It appears reasonable from the observed data to say that the relaxation rate was greater than at 100 per cent elongation, but certainly not more than three times as great. It is possible that for these very high elongations, the valence angles of the long chain molecules were somewhat stretched, thus hastening reaction. For 20, 50, and 100 per cent elongations, the relaxation rates were practically identical.

More general equations for relaxation of stress at constant extension have been derived[8], but for Hevea gum Equation (6) satisfactorily explained experimental results. Secondary network bond relaxation did not appear to be of great importance in Hevea gum at high temperatures.

All the synthetic rubber stocks, gum, and tread studied, including the Buna-S types, the Butaprene-N types, Neoprene-GN, and the Butyl types (see Table IV and Figures 13 to 18), showed behavior in these experiments not far different from that of Hevea. Equation (6) did not apply so well to any of the other stocks as it did to Hevea gum, but the general relaxation behavior was the same. Although the times necessary for nearly complete relaxation of stress varied by about tenfold between the various rubbers, the free energy of activation for the process did not vary from 30.4 kcal. per mole (the value for Hevea gum) by more than ± 2.0 kcal. per mole. This is a strong indication that whatever chemical reaction was responsible for the decay of stress it must have been common to all the rubbers, the slight difference in energies having been caused by the perturbing influence of the side groups which differed in the various rubbers.

TABLE IV

FRACTIONAL STRESS VALUES

Stock No.	Polymer	Type	Temp. (° C)	Fraction of 0.00316-hr. stress at 0.00316 hr.	0.01 hr.	0.0316 hr.	0.1 hr.	0.316 hr.	1.0 hr.	3.16 hr.	10.0 hr.	31.6 hr.
R198	Hevea smoked sheet	Gum	100	1.000	0.987	0.979	0.970	0.960	0.915	0.817	0.627	0.314
R202	Buna-S (GR-S)	Gum	100	1.000	0.980	0.962	0.938	0.900	0.833	0.752	0.652	0.538
R210	Butaprene-NM	Gum	100	1.000	0.975	0.945	0.908	0.865	0.807	0.715	0.598	0.456
R216	Neoprene-GN	Gum	100	1.000	0.923	0.846	0.769	0.678	0.544	0.359	0.198	0.090
4007–2	Butyl B-3	Gum	100	1.000	0.986	0.975	0.960	0.927	0.860	0.731	0.578	0.414
R214	Buna-S 100/0	Gum	100	1.000	0.978	0.954	0.932	0.895	0.842	0.777	0.691	0.574
R200	Buna-S 85/15	Gum	100	1.000	0.980	0.960	0.934	0.900	0.860	0.795	0.695	0.510
R202	Buna-S 75/25 (GR-S)	Gum	100	1.000	0.980	0.962	0.938	0.900	0.833	0.752	0.652	0.538
R204	Buna-S 60/40	Gum	100	1.000	0.955	0.915	0.884	0.829	0.766	0.701	0.628	0.523
R208	Buna-S high conversion	Gum	100	1.000	0.979	0.959	0.937	0.905	0.846	0.755	0.641	0.470
R202	Buna-S med. conversion (GR-S)	Gum	100	1.000	0.980	0.962	0.938	0.900	0.833	0.752	0.652	0.538
R206	Buna-S low conversion	Gum	100	1.000	0.960	0.910	0.857	0.761	0.696	0.606	0.485	0.345
R218	Butaprene-N	Gum	100	1.000	0.988	0.976	0.959	0.924	0.866	0.768	0.640	0.475
R210	Butaprene-NM	Gum	100	1.000	0.975	0.945	0.908	0.865	0.807	0.715	0.598	0.456
R226	Butaprene-NM low fatty acid	Gum	100	1.000	0.988	0.966	0.940	0.890	0.808	0.685	0.537	0.392
R212	Butaprene-NX	Gum	100	—	—	—	—	—	—	—	—	—
R199	Hevea smoked sheet	Tread	100	1.000	0.970	0.938	0.901	0.845	0.765	0.624	0.405	0.166
R203	Buna-S (GR-S)	Tread	100	1.000	0.963	0.922	0.884	0.845	0.797	0.732	0.638	0.495
R211	Butaprene-NM	Tread	100	1.000	0.976	0.950	0.925	0.895	0.850	0.775	0.659	0.512
R217	Neoprene-GN	Tread	100	1.000	0.943	0.883	0.823	0.748	0.648	0.506	0.350	0.206
3861–5	Butyl B-3	Tread	100	1.000	0.975	0.950	0.923	0.878	0.798	0.666	0.505	0.362
R215	Buna-S 100/0	Tread	100	1.000	0.970	0.938	0.908	0.873	0.825	0.750	0.635	0.464
R201	Buna-S 85/15	Tread	100	1.000	0.972	0.940	0.906	0.868	0.823	0.756	0.665	0.512
R203	Buna-S 75/25 (GR-S)	Tread	100	1.000	0.963	0.922	0.884	0.845	0.797	0.732	0.638	0.495
R205	Buna-S 60/40	Tread	100	1.000	0.957	0.910	0.963	0.820	0.760	0.667	0.549	0.419

* Tested in commercial nitrogen atmosphere.

Stock No.	Polymer	Type	Temp. (° C)	Fraction of 0.00316-hr. stress at 0.00316 hr.	0.01 hr.	0.0316 hr.	0.1 hr.	0.316 hr.	1.0 hr.	3.16 hr.	10.0 hr.	31.6 hr.
R209	Buna-S high conversion	Tread	100	1.000	0.968	0.932	0.899	0.857	0.798	0.709	0.583	0.427
R203	Buna-S med. conversion (GR-S)	Tread	100	1.000	0.963	0.922	0.884	0.845	0.797	0.732	0.638	0.495
R207	Buna-S low conversion	Tread	100	1.000	0.955	0.915	0.870	0.825	0.763	0.666	0.548	0.406
R219	Butaprene-N	Tread	100	1.000	0.986	0.962	0.927	0.878	0.809	0.714	0.589	0.434
R211	Butaprene-NM	Tread	100	1.000	0.976	0.950	0.925	0.895	0.850	0.775	0.659	0.512
R227	Butaprene-NM low fatty acid	Tread	100	1.000	0.973	0.944	0.908	0.860	0.779	0.665	0.540	0.386
R213	Butaprene-NX	Tread	100	1.000	0.963	0.923	0.886	0.813	0.740	0.645	0.575	0.480
4007–2	Butyl B-3	Gum	100	1.000	0.986	0.975	0.960	0.927	0.860	0.731	0.578	0.414
3861–4	Butyl B-3	Low black	100	1.000	0.986	0.975	0.957	0.925	0.863	0.745	0.596	0.463
3861–5	Butyl B-3	High black	100	1.000	0.975	0.950	0.923	0.878	0.798	0.666	0.505	0.362
4007–1	Butyl B-1.45	Gum	100	1.000	0.974	0.948	0.923	0.897	0.824	0.711	0.567	0.418
3861–1	Butyl B-1.45	Low black	100	1.000	0.975	0.955	0.929	0.898	0.831	0.707	0.555	0.411
3861–2	Butyl B-1.45	High black	100	1.000	0.970	0.935	0.908	0.864	0.785	0.659	0.508	0.356
R280	Buna-S antioxidant added	Gum	120	1.000	0.964	0.916	0.849	0.739	0.582	0.408	—	—
R278	Buna-S antioxidantless	Gum	120	1.000	0.925	0.843	0.701	0.492	0.283	0.154	—	—
R281	Buna-S antioxidant added	Tread	120	1.000	0.961	0.920	0.874	0.804	0.720	0.577	0.426	—
R279	Buna-S antioxidantless	Tread	120	1.000	0.950	0.895	0.837	0.754	0.618	0.439	0.236	—
R262	Hevea smoked sheet (sulfurless)*	Gum	100	1.000	0.980	0.961	0.943	0.905	0.819	0.690	0.505	0.286
R264	Buna-S (GR-S) (sulfurless)*	Gum	100	1.000	0.963	0.916	0.878	0.820	0.760	0.673	0.555	0.409
R261	Hevea smoked sheet (sulfurless)*	Tread	100	1.000	0.961	0.920	0.874	0.810	0.712	0.563	0.366	0.157
R263	Buna-S (GR-S) (sulfurless)*	Tread	100	1.000	0.935	0.874	0.813	0.744	0.663	0.556	0.426	0.275

* Tested in commercial nitrogen atmosphere.

Table IV gives the ratio of attained stress, at equal logarithmic time intervals, to stress at 0.00316 hour for all of the stocks studied at 50 per cent elongation. This clearly shows that, whereas they were all closely grouped from the standpoint of activation free energy, the corresponding differences observed in the time rate of relaxation for the various polymers were fairly large.

For the case of the synthetic rubbers and for Hevea tread, although Equation (6) did not apply over the entire course of the stress-log time plot as well as it did for Hevea gum, if one assumes that the rate constant k' is equal to the reciprocal of the time that it takes for the stress to reach $1/e$th (36.8 per cent) of its initial value, one can calculate values of $\Delta F^{\ddagger}$ from the data at any given temperature.

The best values of $\Delta F^{\ddagger}$ for Hevea gum and tread and GR-S gum and tread were, respectively, 30.37, 30.05, 31.83, and 31.44 kcal. per mole. Assuming that $\Delta F^{\ddagger}$ is independent of temperature, one can compare the observed and the calculated values for the time it took the stress to decay to 36.8 per cent of its initial value. The close agreement between observed and predicted values is shown in Table V.

TABLE V

COMPARISON OF OBSERVED AND CALCULATED TIMES FOR RELAXING TO $1/e$TH OF INITIAL STRESS

Polymer	$\Delta F^{\ddagger}$ (kcal. per mole)	Temp. (° C)	t_e (calculated)	t_e (observed)
R198 (Hevea gum)	30.37	100	22.6 hr.	26.2
		110	7.50	7.40
		120	2.63	2.55
		130	0.993	0.900
R199 (Hevea tread)	30.05	100	11.7	13.0
		110	4.94	4.60
		120	1.75	1.79
		130	0.841	0.785
R202 (GR-S gum)	31.83	100	162.0	165.0
		110	51.0	46.5
		120	16.9	17.4
		130	6.14	6.40
R203 (GR-S tread)	31.44	100	96.2	85.0
		110	30.8	28.0
		120	10.4	11.5
		130	3.80	4.25

As between the two possibilities of oxidative scission at some point along the chain or spontaneous rupture of the cross-linking bond, comparison of the results of this test with studies of oxidation and aging left little doubt that the postulated primary bond relaxation phenomenon was the result of a reaction of the rubber with oxygen. More experimental evidence, especially in conjunction with chemical studies, is required before the particular type of bond, *i.e.*, the double bond, the carbon atom in an α-position to the double bond, or the cross-linking bond, which is cut by oxygen can be established. Kemp, Ingmanson, and Mueller[9], in a study of the oxidation of vulcanized rubber, found that there was a linear decrease in tensile strength with increase in weight of hydrocarbon resulting from absorption of oxygen. At 4.50 hours at 100° C the tensile strength decreased by half, and the oxygen absorption weight gain

on hydrocarbon was 0.71 per cent. In these experiments the stress in Hevea gum stock decayed to half its initial value in 18 hours.

Experiments such as those of Kemp and coworkers, discussed above, showed that very small proportions of oxygen were effective in completely deteriorating the rubber. This is understandable in terms of the network theory of rubber structure inasmuch as one oxidative cut per chain will break the network completely apart. This is also in agreement with the observation that, in these experiments, rubber bands, completely relaxed at 100° C and for which the tensile strength had become practically zero (by a hand test), showed no gross evidence of oxidation such as stickiness or brittleness. At higher temperatures these physical evidences of oxidation were manifest.

Inasmuch as there was no appreciable difference between the results of these relaxation experiments in air and in commercial nitrogen, we must conclude that the oxidative process occurred at a rate independent of oxygen pressure within these limits. Reed[10] found that aging at 90° C occurred almost as rapidly in commercial nitrogen as in air, but that very little aging occurred in comparable periods if purified nitrogen was used. Morgan and Naunton[11] also found that the rate of oxidation was independent of pressure within these limits.

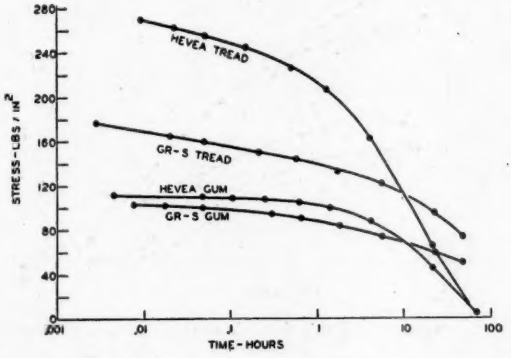

FIG. 13.—Hevea and GR-S stocks; 100° C; 50 per cent elongation.

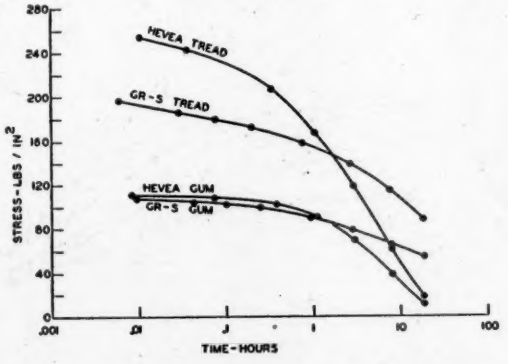

FIG. 14.—Hevea and GR-S stocks; 110° C; 50 per cent elongation.

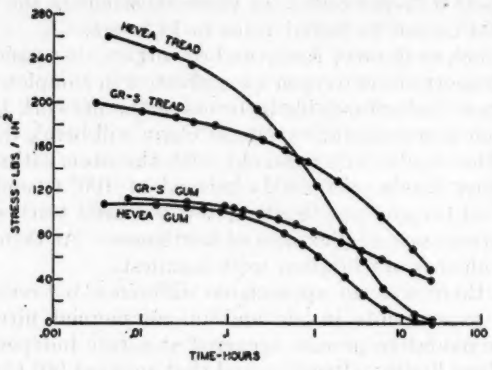

FIG. 15.—Hevea and GR-S stocks; 120° C; 50 per cent elongation.

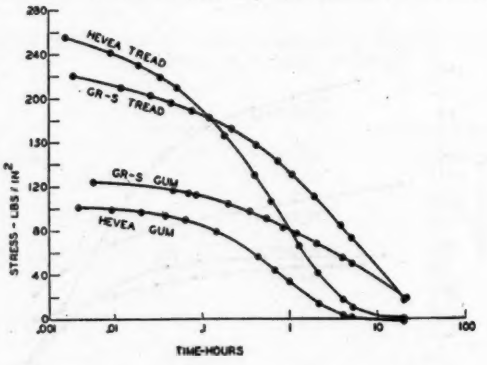

FIG. 16.—Hevea and GR-S stocks; 130° C; 50 per cent elongation.

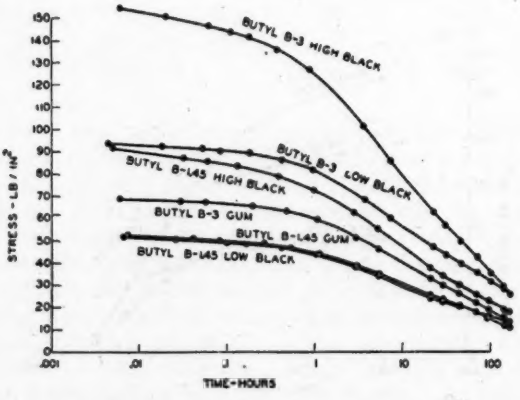

FIG. 17.—Butyl stocks; 110° C; 50 per cent elongation.

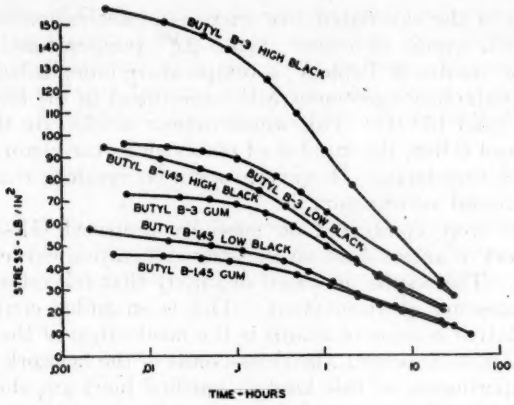

FIG. 18.—Butyl stocks; 120° C; 50 per cent elongation.

The rubber bands which were slightly less than 1 mm. thick were within the limits found by Kemp for which thickness did not affect rate of oxidation. The independence of rate on pressure also indicates that chemical reaction and not diffusion of oxygen through the rubber was the determining factor in these experiments. However, it must be emphasized that of the highest temperatures used, these thicknesses were just barely small enough. Thicker specimens used in these experiments would definitely confuse the results.

Several problems presented themselves as a result of these experiments. If oxidation was the cause of deterioration, which bonds in the postulated network structure did the oxygen attack, the double bonds, the cross-bonds, or perhaps special bonds such as the double bonds adjacent to the cross-bonds. Experiments with Butyl rubber at temperatures of 100° C and 120° C showed that, at least for the polymers used in these studies, the relaxation of stress behavior was very similar to that of GR-S. (Compare Figures 17 and 18 with Figures 13 and 15.) This might, of course, indicate that there is still appreciable residual

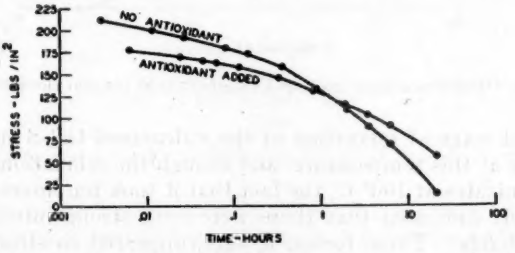

FIG. 19.—Buna-S tread stock; sulfur as stabilizer; 120° C; 50 per cent elongation.

unsaturation in vulcanized butyl stocks, even though only small amounts of butadiene are polymerized with isobutylene in synthesizing the raw Butyl polymer. This amount of unsaturation should, nevertheless, be small compared to that occurring in the other rubbers studied here.

The rate constants defined by Equation (3) and subsequent equations include within them as a multiplicative factor the number of places along the chain that are subject to scission. If this number is larger than unity, it

would show up in the calculated free energies of activation as an entropy of activation, which would of course make $\Delta F^{\ddagger}$ temperature dependent. As was seen by the results of Table V, a temperature independent $\Delta F^{\ddagger}$ appeared to give very satisfactory agreement with experiment in the temperature range between 100° C and 130° C. This would appear to indicate that even for the case of Hevea and GR-S, the number of places along the chain that are subject to scission is not very large. However, such a far reaching conclusion requires further experimental vertification.

Experiments were conducted on specially prepared GR-S stocks to determine the effect of antioxidant on the stress relaxation curves (see Figure 19 and Table IV). The results indicated definitely that relaxation occurred more slowly in the presence of antioxidant. This is an added confirmation of the belief that oxidative scission of chains is the mechanism of the stress decay.

If in the absence of oxygen, the cross-bonds of the network are the weakest bonds, then experiments of this kind in purified inert gas should be of great value in establishing the nature of the rubber structure, but great pains would have to be taken to eliminate all traces of oxygen, both from within and without the sample.

GR-S FILM FROM CCl_4 SOLUTION

The relaxation of a GR-S film prepared by M. Magat of Princeton University, by drying a CCl_4 solution of the polymer is shown in Figure 20. The ten-second stress at 100° C and 50 per cent elongation was 7.46 lbs. per inch (by extrapolation). The time necessary to relax to 36.8 per cent of this value was 0.44 hour. The low initial stress value and the shape of the curve sug-

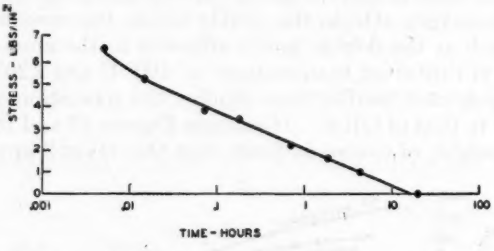

FIG. 20.—GR-S film; sol and gel from CCl_4 solution; 50 per cent elongation; 100° C.

gested the final stage of relaxation of the vulcanized GR-S stocks. The film was not plastic at this temperature, and though the relaxation was more rapid than for vulcanizates at 100° C, the fact that it took ten hours for the stress to relax completely indicated that there were very strong intermolecular forces between the chains. These forces, in fact, appeared so strong as to suggest primary valence forces between the chains. One possible explanation was that oxygenative cross-linking occurred during drying. Another possibility was that the polymer "solution" was really a swollen gel which, on drying, retained in collapsed form its original network structure. The relaxed specimens in these experiments showed definite evidences of oxidation, passing through a tacky and a brittle stage.

In contrast to this behavior, unvulcanized Hevea (in the form of smoked sheet) is very rubbery, with a relatively high modulus and tensile strength at room temperature. At a temperature of 100° C, however, it will not maintain

stress for any length of time, and will flow under small loads as soon as the specimen gets up to temperature. This indicates that the bonds holding the smoked-sheet molecules together are of a secondary nature. This of course agrees with the observation that the smoked sheet used was completely soluble in certain solvents. The GR-S film used above was not resoluble after having been dried.

SECONDARY BOND RELAXATION

Figures 21 and 22 show a compilation of data from stress relaxation measurements on Hevea gum at temperatures ranging between $-50°$ and 150° C. The function g is defined by multiplying the absolute stress in lbs. per sq. in. (at

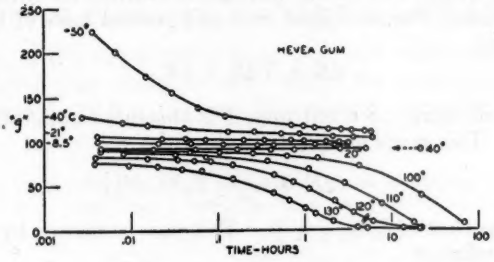

FIG. 21.—g as a function of time for various temperatures.

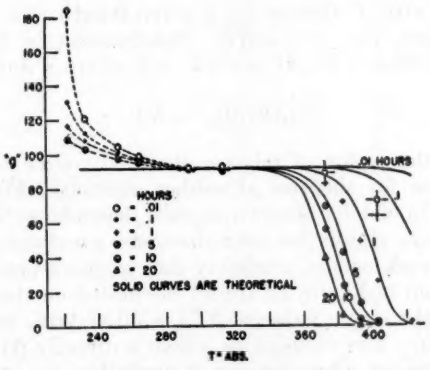

FIG. 22.—g as a function of temperature for various times; Hevea gum.

50 per cent extension) by $298/T$ where T is the absolute temperature. In Figure 21, g is plotted against logarithmic time for various temperatures, the data for each isothermal g curve having been taken in a single experimental run. From the smooth curves obtained, the values of g at any given temperature after 0.01 hr., 1 hr., etc., can be secured. These data have been replotted in Figure 22, where g is shown as a function of the absolute temperature for various times.

If time effects could be neglected, then from Equation (2) it is apparent that g plotted against T (for a definite extension, in this case 50 per cent) should give a constant, *i.e.*, a straight line parallel to the T axis. It is clear from Figure 22 that, in ordinary experimental times of measurement less than

1 hour, g for Hevea gum is practically constant in the range of temperature between 10° and about 90° C. In this region, secondary bonds are unstable in the times of measurement, and primary bonds of the network are breaking at a low rate, so that for stress-strain experiments carried out in reasonable time intervals, Hevea gum behaves nearly like a thermodynamically stable substance for which time effects can be neglected.

The constancy of g with T in this range proves that one of the assumptions on which all kinetic theories of rubberlike elasticity are based is essentially correct. The assumption under discussion is the hypothesis that the internal energy of the Hevea gum rubber is independent of the length for moderate extensions where crystallization is not important, and that the elastic reaction of the network is wholly due to the decrease of entropy on stretching. Mathematically formulated, the combined first and second laws of thermodynamics give the equation:

$$dE = TdS + \tau dl, \tag{8}$$

where E is internal energy, S is entropy, T is absolute temperature, τ is tension, and l is length. This gives on differentiation:

$$\tau = (\partial E/\partial l)_T - T(\partial S/\partial l)_T \tag{9}$$

The hypothesis is that $(\partial E/\partial l)_T = 0$. This can be shown by considering the thermodynamic relation:

$$(\partial E/\partial l)_T = -T(\partial \tau/\partial T)_l + \tau \tag{10}$$

If g is a constant with T then τ for a given length is a constant times the absolute temperature, i.e., $\tau = a(l)T$. Substituting in Equation (10) it is apparent that $(\partial E/\partial l)_T = 0$. If $\tau = aT + b$ where a and b are functions of l, then:

$$(\partial E/\partial l)_T = b(l)$$

In addition to the region of relative thermodynamic stability and its important consequence for theories of rubber elasticity, Figure 22 shows two interesting regions, in which g shows a marked dependence on T as well as time. The high-temperature region has been discussed previously as a region where scission of the network occurs, probably due to small percentages of oxygen. The solid lines shown in Figure 22 are all calculated on the basis of Equations (5) and (4), using the single value of $\Delta F^{\ddagger} = 30.37$ kcal. per mole for the free energy of activation. The value of g_0, which is directly related to the number of chains in the network when scission is negligible, is obtained from the flat region of the curve. The solid calculated curves in Figure 22 are, hence, essentially a one-parameter family, and the coincidence of theory and experiment for the long-time intervals must be regarded as very satisfactory.

For the short-time intervals, the slight deviation existing between theory and experiment can be attributed to experimental procedure. To obtain the desired uniform temperature it is necessary to keep the samples in the oven for about 15 minutes before they are elongated and the first stress reading taken. During this time, especially at high temperatures, an appreciable number of chains are cut. It can be noted from the graph that this explains almost quantitatively the observed deviations. In Figure 22 the points surrounded by radial marks are those for which this consideration is most serious. For the longer times such as 10 or 20 hours, an uncertainty of 15 minutes is naturally less important.

The second region of rapid change of g with T and with time occurs at low temperatures, below 10° C. This is the region where secondary bond formation between the chains becomes important, leading at very low temperatures to the crystalline solid. The secondary bonds between molecules exhibit relaxation phenomena of a reversible nature in contradistinction to primary bond relaxation which is irreversible.

Inasmuch as only the initial portion of the secondary relaxation region has been attained, it is not possible to test whether a relaxation equation of the type given in Equation (7) or the more general relaxation equations recently proposed,[5] which take into account the effect of stress on the rate of breaking of secondary bonds, are suitable for fitting the experimental data.

PRACTICAL IMPLICATIONS OF STRESS RELAXATION

The analysis of the stress relaxations, from the standpoint of the reaction rate theory, showed that all stocks came within the same general region of free energy of activation (30.4 ± 2.0 kcal. per mole). Actually, however, as has

TABLE VI

TIME TO RELAX TO 60 AND 36.8 PER CENT OF TEN-SECOND STRESS VALUE. 50 PER CENT ELONGATION; 100° C

Group	Polymer	Ten-second stress (lbs. per sq. in.)		t_{60} (hours)		$t_{36.8}$ (hours)	
		Gum stock	Tread stock	Gum stock	Tread stock	Gum stock	Tread stock
1	Hevea smoked sheet	112	278	11.0	3.7	24	11
	Buna-S (GR-S)	106	177	18	14	150	81
	Butaprene-NM	158	275	10	16	—	—
	Neoprene-GN	78	245	0.6	1.5	3.3	8.7
	Butyl B-3	69	157	8.7	5	—	—
2	Polybutadiene 100/0	140	352	23	12.5	—	—
	Buna-S 85/15	151	279	20.5	17	54	67
	Buna-S 75/25 (GR-S)	106	177	18	14	150	81
	Buna-S 60/40	53	128	14	6.2	—	43.5
3	Buna-S 75/25 high conversion	144	228	13	8.5	52	47
	Buna-S 75/25 (GR-S) med. conversion	106	177	18	14	150	81
	Buna-S 75/25 low conversion	33	123	3.5	6.4	29	47
4	Butaprene-N	282	393	13	9	75	47
	Butaprene-NM	158	275	10	16	—	—
	Butaprene-NM (low fatty acid)	172	245	6.4	5.8	36	36
	Butaprene-NX	—	254	—	6.8	—	—
5	Butyl B-3 gum	69		8.7		70	
	Butyl B-3 low black	94		9.8		78	
	Butyl B-3 high black	157		5.0		30	
	Butyl B-1.45 gum	53		7.6		53	
	Butyl B-1.45 low black	52		7.2		57	
	Butyl B-1.45 high black	93		5.2		23.5	
6	*Buna-S 75/25 (antioxidant added)	56	213	0.9	2.5	4.2	15
	*Buna-S 75/25 (no antioxidant)	33	183	0.18	1.0	0.66	10.5

* Tested at 120° C.

been mentioned, these variations in energy represent appreciable differences in the time rate of relaxation, differences which may well have practical significance. As an illustration of these differences, Table VI gives the time necessary to relax the stress to 60 per cent and to 36.8 per cent of its value at ten seconds (0.00278 hour) after application of the stress with an elongation of 50 per cent and a temperature of 100° C.

Since it is likely that the stocks have lost their practical usefulness in most service applications when their oxidation has proceeded far enough to cause the

stress to relax to 60 per cent of initial value, only the t_{60} values of Table VI are considered in this discussion.

From the data of Table VI, the following observations may be made:

Group 1.—Of the five basic types of stocks, illustrated by Hevea, Buna-S (GR-S), Butaprene-NM, Butyl B-3, and Neoprene-GN, a difference in time to relax, and thus in relaxation rate, of thirty to one in the gum stock and eleven to one in the tread stock was found. The rapid relaxation rate of Neoprene-GN is to be especially noted.

Group 2.—In the Buna-S type, medium conversion stocks, an increase in styrene content generally increased the relaxation rate for both gum and tread type stocks. One exception was noted in the case of the polybutadiene tread.

Group 3.—In the Buna-S type, 75/25 butadiene-styrene ratio stocks, a minimum relaxation rate was found for the medium conversion gum and tread type stocks.

Group 4.—The rate of relaxation of gum type stocks was slightly increased by modifying the Butaprene-N polymer; that of tread type stock, slightly decreased. Reduction of the fatty acid content of Butaprene-NM increased the relaxation rate in both gum and tread stocks. No significant difference was noted between Butaprene-N and Butraprene-NX in tread stock.

Group 5.—Very little difference was observed between Butyl B-3 and comparable B-1.45 stocks. The high black stock in both types had a somewhat higher relaxation rate.

Group 6.—In Buna-S stock, compounded with polymer prepared without antioxidant, but with sulfur as a stabilizer, the addition of an antioxidant to the compound definitely retarded the relaxation rate.

If the rate of relaxation is, in fact, a function of the oxidation of the stock as has been suggested, it becomes a very convenient tool for the study of the oxidizability of natural and synthetic-rubber stocks, and the trends shown in Groups 1 to 6 may well serve as indices of oxidizability. Since the rate of relaxation has been shown to the practically independent of the elongation from 700 per cent to as low as 20 per cent, this index would appear to assume significance even in cases of stocks with applications involving no steady strain. It is very likely that a distinction should be made between the early part of the curve, during which it has been postulated that secondary bonds are primarily responsible for the effect, and the latter part of the curve, which is believed to be largely governed by the severing of primary bonds. In a suitable temperature range, the experimental time interval may well include parts of both these regions. For example, Hevea, compred with GR-S, had a relatively low initial rate of relaxation, a relatively high final rate. Other examples may be found in Table IV. Thus it is apparent that the entire curve should be studied in the suggested analysis of stock oxidizability.

The way in which the rubber structure is attacked by oxygen is important both from a practical and theoretical standpoint. It is well known that oxygen has two effects on rubberlike polymer systems. One effect that has been stressed in this study is oxidative scission; the other is a cross-linking oxidation phenomenon. Most frequently these reactions occur simultaneously, and in some cases the cross-linking effect follows very closely after scission. The physical appearance of the samples exposed to air at high temperatures in the relaxation apparatus is indicative of this behavior, some samples going through a tacky stage and then a brittle stage. The tackiness is of course to be associated with scission of chains and stress decay. In the case of natural rubber the tacky range is quite large; in the case of GR-S, quite transient. It appears

that, occurring simultaneously with the scission of chains, a cross-linking reaction occurs which tends to produce hardness and brittleness. This reaction is initially slower than the scission reaction in Hevea, but in GR-S the hardening reaction is always faster. The physical appearance of specimens of Hevea and GR-S in the temperature box for 20 hours at various temperatures is shown in Table VII. These varying behaviors for different type stocks may have

TABLE VII

CHANGE IN PHYSICAL APPEARANCE OF RING SAMPLES AS A FUNCTION OF TEMPERATURE AFTER 20 HOURS AT 50 PER CENT ELONGATION

Polymer	Stock type	Temperature of test (° C)	Change in appearance after treatment
Hevea	Gum	110	Slightly tacky
		120	Tacky
		130	Very brittle
	Tread	110	No change
		120	Slightly tacky
		130	Very brittle
GR-S	Gum	110	No change
		120	No change
		130	Quite brittle
	Tread	110	Slightly hard
		120	Slightly hard
		130	Brittle

important implications in the wearing and cracking of rubber articles, such as tires, subjected to stress at high temperatures.

The importance of the relaxation of stress method is that it measures exclusively the rate of chain cutting at high temperatures. Inasmuch as the cross-linking occurs between relaxed chains, this chemical phenomenon is not reflected in the physical measurement of stress decay at constant elongation.

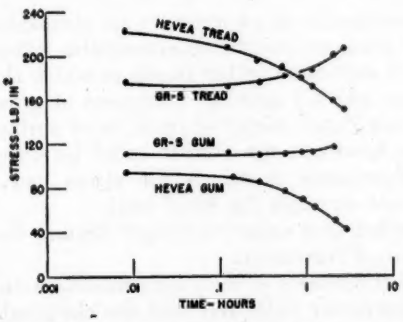

FIG. 23.—Stress required to attain 50 per cent elongation; intermittent measurements, 130° C.

If instead of keeping the rubbers at constant elongation, they are left in a relaxed state and the stress required to elongate these a definite amount is measured from time to time, then the net rate of cross-linking minus chain scission is measured. In the case of Hevea gum and tread, the stress required to attain a certain elongation (50 per cent at 130° C for this experiment) decreases as a function of time, though not quite so rapidly as if the elongation

were maintained constant. In the case of GR-S gum and tread stocks, the stress required to attain 50 per cent elongation at regular intervals increased as a function of time, indicating that the cross-linking reaction is faster than scission for these rubbers. This of course agrees with the observations of the physical appearance of the samples. The results of this experiment are shown in Figure 23, which should be compared with Figure 16.

SUMMARY

1. The complete decay of stress in the rubbers studied, held at constant elongation, appeared to involve the rupturing of a definite bond, either at some point along the molecular chain or at the cross-linking bond put in by vulcanization. In the case of a Hevea rubber gum stock the data could be fitted very well by ordinary reaction-rate theory, leading to the conclusion that the free energy of activation required for breaking the bond is 30.4 kcal. per mole of bonds. This result was found to be practically independent of the elongation, and of the presence of carbon black in a Hevea rubber tread stock. This is to be compared to a strength of about 90 kcal. per mole for the C−C bond.

2. In the case of other rubbers (Buna-S, Butaprene-N, Neoprene-GN, and Butyl) the activation free energy for breaking the bond did not vary by more than ±2.0 kcal. per mole from that of Hevea rubber. However, these differences were quite definite. For example, the relaxation of stress in GR-S was slower than in Hevea; a small difference in energy corresponding to a 2:1 ratio in the respective times of decay.

3. The effect of temperature on the relaxation of stress appeared to be of the general type characteristic of chemical reactions. By use of the ordinary formula for expressing rate of reaction in terms of energy of activation, one could predict very closely the behavior of the stress-log time curves at different temperatures.

4. Natural rubber and GR-S vulcanized with paraquinone dioxime and lead dioxide showed relaxation curves very similar to those of the sulfur vulcanized stocks.

5. Relaxation experiments in an ordinary air atmosphere and in an atmosphere of commercial nitrogen showed no appreciable differences.

6. Examination of stretched rubber bands in which the stress had decayed nearly completely (at 100° C) gave no evidences of gross oxidation, such as would make the rubber bands sticky or hard, or of surface deterioration. At higher temperatures, however, the rubber could be observed getting sticky, and then brittle. Specimens in which the stress had completely decayed showed very low tensile strength (by hand test).

7. Antioxidant added to a sulfur-stabilized Buna-S stock caused a definite retardation of the rate of relaxation.

8. Comparison of the results of these experiments with previously recorded observations in the literature indicated that the chemical reaction which ruptured the rubber structure and caused the decay of stress in these experiments (and concomitantly a lowering of tensile strength) was an oxidation of the rubber by small amounts of oxygen, the reaction rate being independent of the oxygen pressure in the range between that present in an ordinary air atmosphere and in a commercial nitrogen atmosphere.

9. The tests suggested a convenient and accurate laboratory method of determining the oxidizability of natural and synthetic rubber stock designed for service.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of The Firestone Tire & Rubber Company and Princeton University for making possible this program of cooperative research. Personal thanks are due J. N. Street of Firestone and H. S. Taylor and H. Eyring of Princeton for encouragement and very useful discussion.

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DRIFT AND RELAXATION OF RUBBER *

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INTRODUCTION

Numerous studies have been published on the relaxation and drift, or creep, of soft vulcanized rubber. In the present work, tests of this kind have been extended considerably beyond previously published work, both as to duration of the test and range of the initial stress or elongation. Some compression drift tests have now been in progress for eight years. A new method of measuring stress relaxation at fixed elongation has been developed, particularly with the purpose of conserving space. This method has made it possible and practical to carry out a large number of tests, many of them lasting for many months. An additional advantage of the test is that the samples can be kept in a controlled atmosphere as well as at a controlled temperature.

Some of the more extensive relaxation data have been used to test the Tobolsky-Eyring theory of relaxation. Good agreement is obtained by assuming two relaxation mechanisms. An alternative or modified theory of relaxation is presented.

8-YEAR COMPRESSION DRIFT

One unit of the equipment used in these tests is shown in Figure 1. The sample consists of a rectangular block of rubber *1*, approximately 1 inch thick and 1.5 × 1.5 inches square. It is compressed between two parallel steel plates, *2* and *3*. The rubber is not cemented to the plates. The compressing force, produced by the weighted beam *4*, is applied through knife edge *5*. The fiducial point for measuring the thickness of the rubber is the top of plate *6*. The dial gauge *7* has two steel balls in its base, which rest in a V-groove cut in plate *6*; the stem of the gauge extends down through holes in the intervening parts to rest on the steel ball *10* in the top of plate *3*. With the gauge in this position, the dial is above the top of the wooden box enclosing the drift units. The temperature of the box is maintained at 35° C.

The load on each sample was chosen to produce about 15 per cent compression. In starting a test, the loaded beam was let down on the sample, and was then leveled as quickly as possible by means of adjustment nuts *9*. The first thickness measurement after loading was obtained in less than one minute, and the subsequent drift was based on the one-minute reading taken as the initial value. The gauge is graduated in 0.001 inch; and the tenths of a division are estimated.

D_m, the relative drift with respect to the deformation at 1 minute is calculated according to the equation:

$$D_m = (H_m - H_t)/(H_o - H_m)$$

* Reprinted from the *Journal of Applied Physics*, Vol. 15, No. 4, pages 324–337, April 1944.

in which H_o = the unloaded height, H_m = the height at one minute, H_t = the height at any subsequent time.

These drift samples are subjected to a continuous, slight vibration from the fan motor, and to vibrations transmitted through the floor from machines in the building. The drift box has been moved several times. At each move the beams were supported or steadied to prevent or limit the oscillation. Such

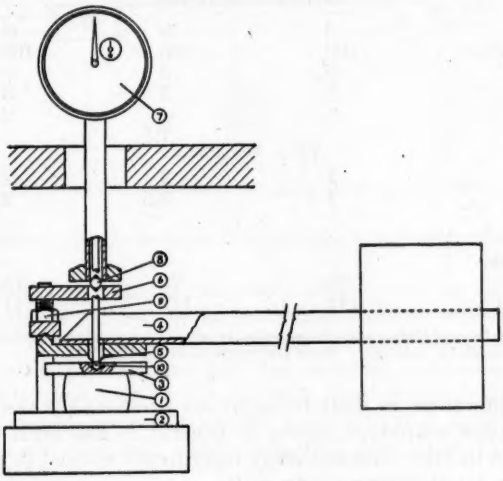

FIG. 1.—Compression drift unit.

oscillations as occurred did not affect the readings seriously. At present the exposed surfaces of the samples are all cracked, at least to some extent, some of them badly. The side controus are decidedly curved, and the surfaces in contact with the steel plates have expanded more or less proportional to the degree of compression. No attempt was made to make the box containing the apparatus light-tight, but the amount of stray light in the box is small.

The data that have been obtained are shown in Figure 2. Stock formulas are given in Table I. Many more observations were made than are reported here. The values given are interpolations between nearest observed points.

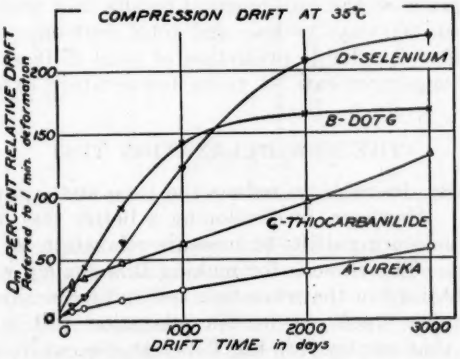

FIG. 2.—Compression drift curves.

In general, the curves rise rapidly at first and then gradually approach a line of constant slope. Exceptions to this behavior are stocks *D* and *B*, after 1000 days. In these cases the drift is so great that the area of the sample has been appreciably increased and the stress correspondingly reduced.

TABLE I

STOCK FORMULAS

Stock No.	*A*	*B*	*C*	*D*
Smoked sheet rubber	100	100	100	100
Zinc oxide	5	5	5	3
P-33 black	3	3	3	—
Thiocarbanilide	—	—	2	—
D.O.T.G.	—	1.5	—	—
Ureka	.75	—	—	—
VGB	2	2	2	—
Sulfur	2.5	2.5	2.5	3
Laurex	1	—	—	—
Vandex	—	—	—	.2
Aldehyde-ammonia	—	—	—	1
Curing time (min.)	75	75	75	90
Curing temp. (° C)	141	141	141	141

Compounds *E* and *F* are of high-quality commercial type, with no reclaimed rubber. *F* has some carbon black in it, *E* only enough for coloring. Shore Durometers are *E*, 40; *F*, 48.

The large differences in drift revealed are presumably associated with the type of acceleration employed, since, in general, it has been found that such minor differences in other compounding ingredients as exist in these stocks give rise to relatively small differences in drift.

We refer to the early rapid change in height as transient drift; and to the slow change at a practically constant rate as steady drift. A good fit to these curves (excepting the flat portions of *B* and *D*) is given by the empirical equation:

$$D_m = A[1 - \exp(-at^n)] + Bt \qquad (1)$$

in which the term with coefficient *A* represents the transient drift and *Bt* represents the steady drift. *t* is not the time after loading, but the time measured from the reference time, 1 minute after loading. *A*, *a*, and *B* vary considerably with the compound. *n* varies only slightly and is approximately 0.20.

Transient drift remains finite at infinite time, while steady drift becomes infinite. It appears from the experimental results that transient drift is practically completed in 200 days or less; and total drift after 5 years or more is mostly steady drift. A reliable prediction of total drift at 5 to 10 years apparently requires measurements at room temperature extending up to one year or more.

THE NEW RELAXATION TEST

Obviously it was desirable to reduce the time and equipment required to make a drift test. However, in developing a better test method, it was decided, instead of measuring drift, to measure relaxation, or decrease in stress at constant strain. The reasons for making this change will be apparent in the advantages obtained in the relaxation test to be described.

The test-specimen employed in the relaxation test is a square-headed dumbbell, such as that employed in the T-50 test, die-cut from a sheet of rubber about 0.10 inch thick. The heads of the dumbbell are ¼ inch square; the

shank is 2 inches long and 0.075 inch or 0.100 inch wide. Such a sample can be held at any elongation up to 75 per cent or more of the breaking elongation simply by supporting the heads in a pair of hooks or slots. A rack for supporting six samples at the same length is shown in Figure 3. If desired, such a rack

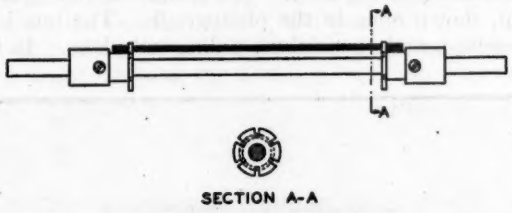

FIG. 3.—Rack for relaxation samples. One sample is shown stretched in the rack.

can be sealed inside a glass tube in any desired atmosphere without interference with the test.

A sample held in one of these racks can vibrate; and the natural frequency of vibration is determined by the length of the sample between supports, by its linear density, and by the tension. Since the first two of these factors remain constant during a relaxation test, the decrease in tension with time can be quite accurately measured by determining the decrease in the frequency of vibration. This is done by mounting the specimens in a mechanical oscillator with a continuously variable frequency, and observing the frequency of maximum resonance.

A schematic drawing of the mechanical oscillator is shown in Figure 4. The bar *1*, on which the rack containing the samples is mounted in a pair of V-

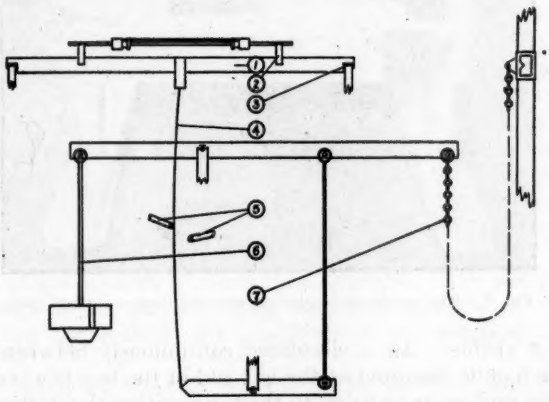

FIG. 4.—Schematic drawing of the mechanical oscillator.

supports *2*, rocks on a pair of colinear knife edges *3*, one at each end. The rocking oscillations in the bar are induced by the loaded steel wire *4*, which is maintained in circular vibration by a pair of air jets *5*, set at 90° with respect to each other and slightly staggered vertically. Each jet is directed approximately along a line tangent to the circular path of the wire. It is sometimes necessary to pluck the wire to start the vibrations, but after that the vibrations

continue at a uniform amplitude. The stress in the wire, and consequently the frequency of vibration, is roughly adjusted by one-pound weights supported on the hook *6*. Fine adjustment is made by the chain *7*.

A photograph of the oscillator, Figure 5, shows a number of details in addition to those mentioned in Figure 4. The oscillating bar is mounted in a box with a glass top, shown open in the photograph. The box is approximately square in cross-section and opens along a diagonal plane. In back of the box

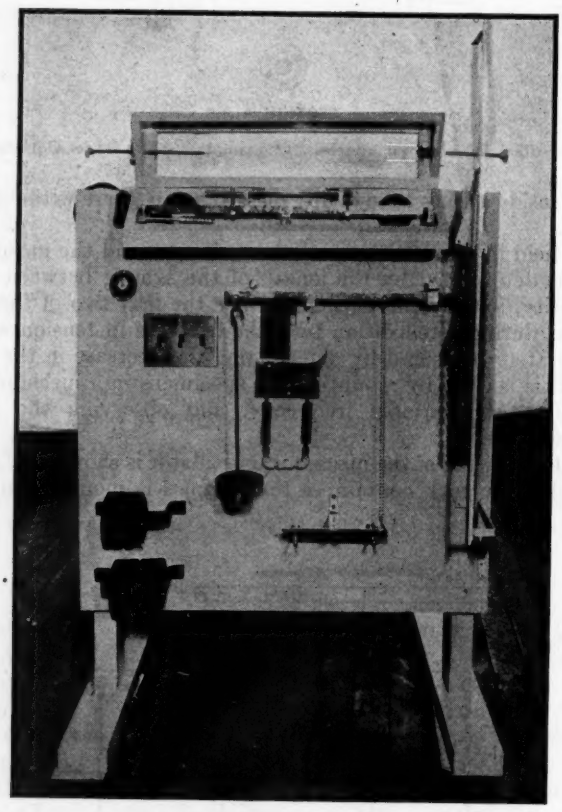

FIG. 5.—The mechanical oscillator, with the thermostat box open.

is an oven, not visible. Air is circulated continuously between the oven and the box. The handle mounted at the left end of the box is a screw-driver tool for rotating the rack so as to bring to the top position the particular sample to be measured. The handle at the right end of the box serves a similar purpose when the rack is sealed inside a glass tube. In this case a metal strap attached to the tube has studs which engage the fork on the handle. When measurements are being made, a Bausch & Lomb shop microscope resting on the glass cover is used to observe the vibration of the test-piece. It has been found very helpful to have attached to the nose of the microscope a flashlight bulb mounted in a flashlight reflector, the two being so arranged that the light of the bulb is brought to a focus approximately at the focal point of the microscope. Vibra-

tion of the test-piece is made more visible by marking on the test-piece with an aluminum pencil at the beginning of the test.

The metal box near the middle of the wire contains a neon lamp which, connected to a 60-cycle current, serves as a stroboscope for calibrating the frequency of the wire. This calibration is more accurate than the calculation of the frequency from the length, density, and tension.

The natural frequency of vibration of either the steel wire or the rubber sample is given by an equation of the form:

$$n = \frac{1}{2\pi L}\left(\frac{gT}{\rho}\right)^{\frac{1}{2}}, \tag{2}$$

in which n = fundamental frequency, in cycles per second, T = tensile force, L = length, ρ = linear density, and g = acceleration of gravity. At resonance we then have:

$$\frac{T_r}{L_r^2\rho_r} = \frac{T_w}{L_w^2\rho_w} \tag{3}$$

where the subscripts r and w refer to the rubber and to the wire, respectively. It then follows that for each specimen $S_\tau(t)$, the relative stress is:

$$S_\tau(t) = \frac{T_r(t)}{T_r(\tau)} = \frac{T_w(t)}{T_w(\tau)} \tag{4}$$

ρ signifying the reference time, or time of the first reading, and t any later time.

Relative relaxation $R(t)$ is:

$$R_\tau(t) = 1 - S_\tau(t) = \frac{T_w(\tau) - T_w(t)}{T_w(\tau)} \tag{5}$$

The practical advantages of this relaxation test are now apparent. The precision is good, measurements to 0.1 per cent on gum stocks being possible. The specimens are small, can be moved about without affecting the tension or elongation, and can be stored in any oven or cold box between measurements.

In the relaxation measurements reported below, the reference time τ is taken as 5 minutes. It generally requires something under 5 minutes to make the first tension measurements on the six samples in one rack. The second measurements are made immediately and in the same sequence; and the 5-minute figure is then obtained by interpolation or extrapolation.

Calculation of the absolute value of initial tension of the test-piece requires the linear density of the sample. This was determined after completion of the test by cutting the heads of the dumbbells off and weighing the shank.

RELAXATION AS A FUNCTION OF TEMPERATURE AND ELONGATION

A program of work was undertaken to study the fundamental nature of relaxation. Among the more important variables studied were elongation and temperature. Information concerning the stock employed is given in Table I, compound *E*. Elongations were from 10 to 400 per cent and the temperatures were 35 and 70° C. The samples were kept in air and were exposed to light only at intervals when taken out of the oven for measuring in the mechanical oscillator. Some samples were stretched to 300 per cent for one minute before bringing them to the elongation in the relaxation test. This

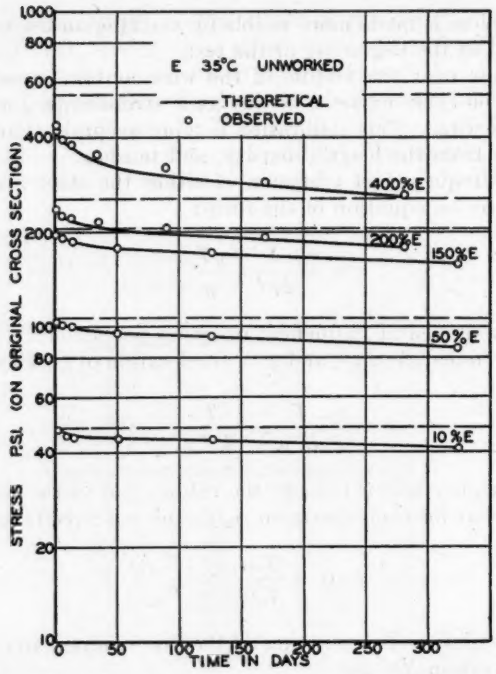

FIG. 6.—Stress relaxation on unworked samples at 35° C, Compound *E*.

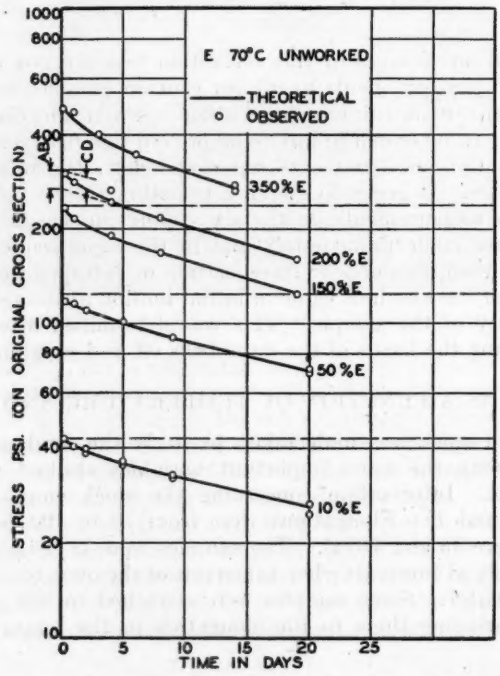

FIG. 7.—Stress relaxation on unworked samples at 70° C, Compound *E*.

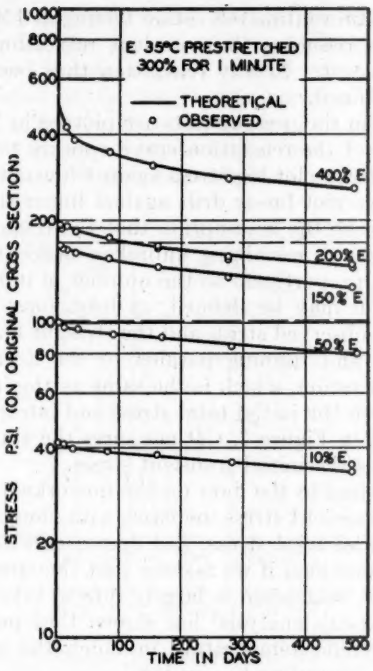

FIG. 8.—Stress relaxation on prestretched samples at 35° C, Compound *E*.

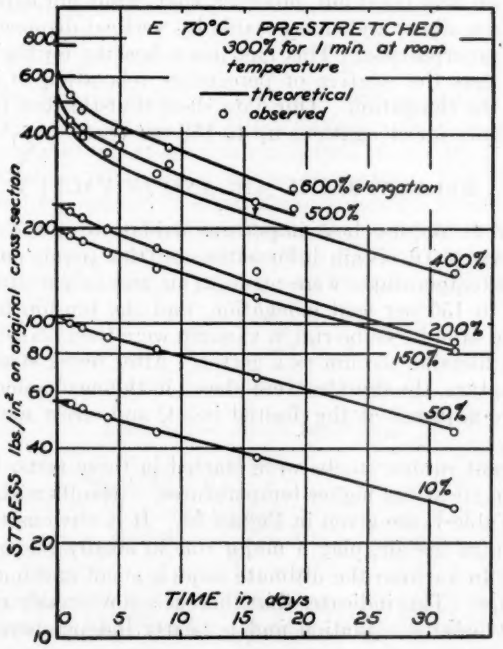

FIG. 9.—Stress relaxation on prestretched samples at 70° C, Compound *E*

procedure, used in certain routine relaxation testing at 150 per cent elongation, was found effective in reducing the transient relaxation occurring after the start of the relaxation test. Steady relaxation thus became more prominent and more easily determined.

The data obtained in the present tests are plotted in Figures 6 to 9. Here we find that the slope of the relaxation curve appears to approach eventually a constant value, when we plot log stress against linear time; whereas the like is true of drift when we plot linear drift against linear time. These two laws are both in harmony with the assumption that the remaining modulus is proportional to the number of remaining unbroken molecular sections, and that the rate of breaking is proportional to the number of unbroken sections.

Transient relaxation may be defined, at least for rough analysis, as the difference between the observed stress and the straight line passing through the point of initial stress and running parallel to the asymptotic tangent line. Ultimate transient relaxation, which is the same as the initial transient stress, is the difference between the initial total stress and intercept of the tangent on the stress axis. Thus, in Figure 7, CD measures the transient relaxation at 2 days, and AB measures the initial transient stress.

We see that, according to the data on the unworked samples, *i.e.*, not prestretched, the initial transient stress increases with elongation, both absolutely and relative to the initial total stress, and decreases with increasing temperature. This can be understood if we assume that the stress component subject to rapid, *i.e.*, transient, relaxation is largely due to crystallites formed in the stretched rubber; for x-ray analysis[1] has shown that percentage crystallinity varies with elongation and temperature in much the same manner as does initial transient stress, according to our data.

A detailed theoretical analysis of our relaxation data is given in a later section. Here we may point out, however, that, while our experimental curves for the lower elongations are superposable by vertical displacement, the other curves are not superposable. This fact has a bearing on the assumption frequently made, that the relative or percentage relaxation of a given stock is independent of the elongation. Our data show that this law is valid as a good approximation only for elongations up to 150 per cent.

RELAXATION IN AIR AND IN VACUUM

It is natural to inquire how important oxidation of the rubber is in the relaxation process. To obtain information on this point, some comparative tests at various temperatures were made in air and in vacuum. The samples were stretched to 150 per cent elongation, and the tension at 5 minutes was measured. The samples to be run in vacuum were then sealed in an evacuated glass tube with metallic sodium as a getter. After being stretched for 1 hour at room temperature, the samples were placed in the mechanical oscillator, with the temperature adjusted at the desired point, and stress measurements were resumed.

Three different rubber stocks were started in these tests, but two of them broke quickly in air at the higher temperatures. Results with the third stock, compound *F*, Table I, are given in Figure 10. It is obvious that air, and presumably oxygen in the air, play a major role in steady relaxation at elevated temperatures. In vacuum the ultimate slope is small and increases very little with temperature. This indicates that there is a slow steady relaxation process which does not involve oxidation and is nearly independent of temperature.

However, a transient relaxation which persists for the duration of the test cannot be ruled out; for the data in this case are insufficient to determine definitely whether the ultimate slope of the log stress curve is zero or finite.

It is surprising to find in the data that at elevated temperatures the initial rate of relaxation in vacuum is higher than it is in air. (This effect is shown in the curves for 70° C, and it exists at the higher temperatures also, even though the scale of the curves is not such as to show it for the higher temperatures.)

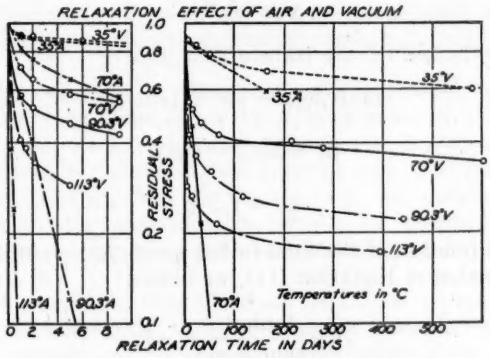

FIG. 10.—Stress relaxation in air *A* and in vacuum *V* at 150 per cent elongation, on unworked samples, Compound *F*.

Also strange is the fact that the ultimate transient relaxation in vacuum is so greatly increased by temperature. The explanation of these results is unknown. Possible factors are peroxides left in the rubber at the beginning of the test, and the well-known reversion of most stocks in prolonged cure.

THEORETICAL ANALYSIS BY THE TOBOLSKY–EYRING EQUATION

The relaxation data of Figures 6 to 9 were first considered in the light of the Kuhn theory[2], assuming several stress mechanisms in parallel. However, according to this theory all relative stress curves should be the same function of time and should consequently be superposable. The Tobolsky-Eyring theory[3] was, therefore, applied in hopes that its dependence of slippage rate on stress might be able to describe satisfactorily the observed curves. In accordance with this theory we write the total stress f at any moment as the sum of two components, f_s and f_t, the steady denoted by subscript s and the transient by subscript t:

$$f = f_s + f_t \tag{6}$$

in which

$$\tanh b_s f_s = 10^{-\alpha_s t} \tanh b_s f_{so} \tag{7}$$

$$\tanh b_t f_t = 10^{-\alpha_t t} \tanh b_t f_{to} \tag{8}$$

where

$$b_i = \lambda_i / 4 N_i k T \tag{9}$$

$$\alpha_i = 0.8686 \frac{n_i \lambda_i k T G_i}{h} \exp - \left(\frac{\Delta F_i}{kT} \right) . \tag{10}$$

f_i is the stress component due to units of type s or t, f_{io} is f_i at $t = 0$, k is Boltzmann's constant, h is Planck's constant, T is absolute temperature, ΔF_i

is the free energy of activation for the slippage mechanism, N_i is the number of stress-bearing units per square centimeter of type i, n_i the number of points of possible slippage per centimeter along the unit, λ_i is the distance jumped by each unit at each slip projected onto the direction of the stress, and G_i is the modulus of component i.

To facilitate the process of fitting the theoretical curves to the data, we express a remaining stress component as a fraction y of its initial value, thus:

$$y_i = f_i/f_{io}$$

Then Equations (7) and (8) are transformed into

$$\tanh \beta_i y_i = 10^{-\alpha_i t} \tanh \beta_i \tag{11}$$

where

$$\beta_i = b_i f_{io} = b_i \zeta_i f_o \tag{12}$$

where

$$\zeta_i = f_{io}/f_o$$

and is the initial fraction of the total initial stress, f_o, comprising the ith type. Taking the logarithm of Equation (11), we obtain:

$$\log \frac{\tanh \beta_i}{\tanh \beta_i y_i} = \alpha_i t \tag{13}$$

This equation shows that, if experimental values of y_i obey the Tobolsky-Eyring theory with a given value of β_i, then a value of the logarithm in Equation (13) calculated from the data will be proportional to the corresponding time. Figure 11 shows, for a series of value of β, log y plotted against log log (tanh β/tanh βy_i). The highest curve in the figure, that for $\beta = 0$, corresponds to a straight line in a plot of log y *vs.* t.

We now let

$$\begin{aligned} Y &= f/f_o \\ \zeta_s &= f_{so}/f_o \\ \zeta_t &= f_{to}/f_o \end{aligned} \tag{14}$$

Then

$$\begin{aligned} Y &= \zeta_s y_s + \zeta_t y_t \\ \zeta_s + \zeta_t &= 1 \end{aligned} \tag{15}$$

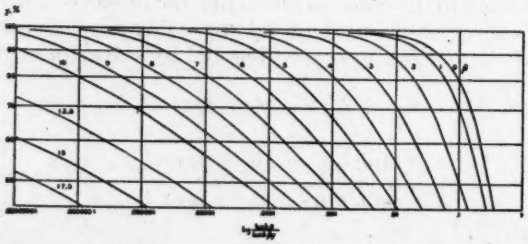

FIG. 11.—Curves of constant β. If remaining (unrelaxed) stress associated with one type of relaxation is plotted against time, the data, after the proper vertical and horizontal shift, should fit one of these curves.

For sufficiently large values of t, the transient stress y_t will be sufficiently small to be neglected in this equation. Consequently, if we plot the observed Y against t on the same scales used in Figure 11, the right end of the experi-

mental curve should fit the right end of one of the theoretical curves of Figure 11. To obtain this fit, the experimental curve may be displaced both horizontally and vertically with respect to the theoretical curves. β_s is the β-value for the theoretical curve giving the best fit. The horizontal displacement determines α_s. The vertical displacement determines ζ_s, ζ_s being equal to the value of Y which coincides with $y = 1$ on the β curve.

The parameters β_s and α_s being thus determined, y_s can be calculated for each observation by means of Equation (13), or can be read from the complete curve for β_s of Figure 11. With y_s and ζ_s determined, $y_t\zeta_t$, which will be the difference between Y and the steady partial stress $y_s\zeta_s$, can be calculated by Equation (15).

The arithmetic residuals, $Y - \zeta_s y_s$, can now be plotted log-log. Then by finding the curve of best fit in Figure 11, β_t is determined. In doing this the curve of residuals may be shifted horizontally at will; but with the assumption of 2 relaxation terms, the vertical shift must be such that the initial value of the residual, $Y = \zeta_s y_{s0}$, which is also ζ_t or $1 - \zeta_s$, will coincide with $y = 1$ in Figure 11. If a third relaxation term were to be assumed or admitted, a vertical shift downward from this position of the residual curve would be allowed in finding the best fit.

Practically, it was found that the β-curves in the experimental range experienced were not sufficiently different in shape (considering reproducibility of experimental conditions) to give a unique assignment to the different parameters of the equation. Several restrictions were, therefore, imposed to reduce the number of degrees of freedom. In most trials α_s and α_t were held constant for all elongations. In method A, ζ_s was constrained to be constant, independent of elongation. A satisfactory fit was found possible by conceding that transient relaxation had only just begun to disappear by the end of the experiment. This type of fit gave activation energies of 38 kg. cal. for steady relaxation and 22 kg. cal. for transient. This analysis was distrusted, however, for two reasons: first, because it required that transient relaxation be not very transient, and because the assumption that the fraction of the transient component ζ_t remains independent of elongation did not agree very well with the data.

In method B, β_s was assumed to be $\ll 1$. For such a case ζ_s is immediately given by the Y intercept of the asymptotic tangent of a plot of log Y *versus* t.

The assumption, implicit in this method, that $b_s \ll 1$ was open to question. To examine this point critically, method C was devised. In this method we first attempt to obtain a unique assignment of b_s by differentiating log y of Equation (11) with respect to time. This gives:

$$d \log y_s/dt = -\alpha_s F(x) \tag{16}$$

where

$$F(x) = \frac{x}{(1 - x_c) \tanh^{-1} x}$$

$$x = 10^{-\alpha_s t} \tanh \beta_s \tag{17}$$

If the accuracy of measurement of the long-time slope of the lowest elongation curve be sufficient to give a good value of α_s, then it is possible to compute values of $F(x)$ by Equation (16) from the long-time slopes of the higher elongation semilogarithmic plots. From such values of F one may work up values of x from a curve of $F(x)$ *versus* x and derive therefrom values of β_s. This method

was disappointing in that the value of α_s, computed from the last pair of points of the lowest elongation curve, did not give a relaxation rate which seemed to fit well the preceding points of the curves on the log-log plot. As modification of this method, therefore, α_s was determined from the log-log plot for $\beta_s = 0$ for the curves of lowest elongation; and this α_s was used in computing F; and thence β_s for curves of higher elongation. This method of unique assignment of β_s gave values in accordance with the hypothesis used in method B, that b_s is negligible.

Assignment of β_s by method C does not turn out to be of much value in determining β_t, because the residuals from the lowest elongation curves are of the same order of magnitude as the precision of experimental conditions. This means that a trustworthy value of α_t may be obtained only from the

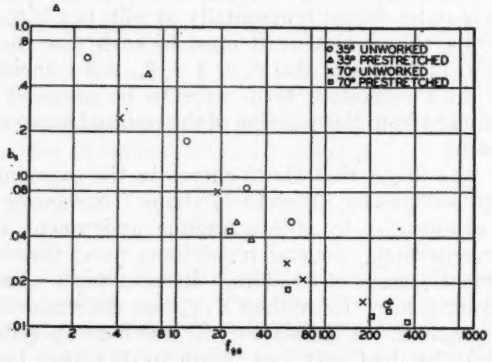

FIG. 12.—Variation of b_t with f_{to}. f_{to} is the initial stress of transient relaxation. Its variation is due mostly to variation in elongation. $b_t = \lambda_t/4N_1kT$, Equation (9).

greatest elongation curves. Therefore, the method chosen for assignment of each β_t in transient relaxation was to find the β-curve with the greatest resemblance to the curve of residuals when ζ_t is made equal to $1 - \zeta_s$. From these independent β_t-values, b_t may be computed for each initial stress. It was found to vary inversely with elongation or with f_{to}, as shown in Figure 12. The curves drawn in Figures 6 to 9 are theoretical curves derived by method C. Values assigned to the parameters are given in Table II.

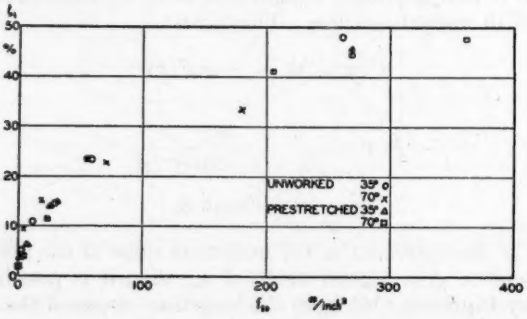

FIG. 13.—Variation of ζ_t with f_{te}. f_{te} is the initial stress of transient relaxation. Its variation is due mostly to variation in elongation. ζ_t is the transient fraction of the initial total stress.

As shown in Figures 12 and 13, ζ_t increases and b_t decreases with f_{to}, or with elongation. It was suggested above that ζ_t increases because of the increase in crystallinity with elongation. If we assume that N_t, the number of transient bonds per sq. cm., is equal to or is proportional to the number of

TABLE II

RELAXATION CONSTANTS—STOCK E

		35°			70°	
		Unworked				
α_s		0.000138			0.0089	
α_t		0.005			0.064	
Relaxation time						
Steady		3150 days			49	
Transient		87			7	
Elongation	f_0	b_t	ζ_t	f_0	b_t	ζ_t
10%	48	0.614	0.051	43	0.245	0.095
50	107	0.173	0.108	124	0.080	0.152
150	204	0.085	0.145	239	0.027	0.233
200	253	0.051	0.233	309	0.021	0.228
350				541	0.015	0.333
400	545	0.014	0.48			
		Prestretched				
α_s		0.00017			0.0106	
α_t		0.0036			0.044	
Relaxation time						
Steady		2560 days			41	
Transient		121			10	
Elongation	f_0	b_t	ζ_t	f_0	b_t	ζ_t
10%	42	1.325	0.036	56	?	0.02
50	101	0.478	0.062	105	?	0.04
150	180	0.050	0.140	199	0.044	0.115
200	213	0.038	0.149	238	0.018	0.235
400	591	0.015	0.456	501	0.012	0.41
500				605	0.013	0.445
600				760	0.011	0.475

Heat of activation, kg. cal.

	Unworked	Prestretched
Steady	25.0	24.8
Transient	15.3	15.0

Note: b_s is too small for determination.

crystallites, and that f_{to}, the initial transient stress, is also proportional to the number of crystallites, then by Equation (9):

$$b_t = \lambda_i/4kTCf_{to} \tag{18}$$

This equation is in good agreement with the empirical relationship between b_t and f_{to} shown by Figure 12.

The data of Figure 10, showing relaxation in air and in vacuum at various temperatures, were also analyzed by the general procedure outlined above. In this case the lack of data at elongations other than 150 per cent makes the determination of the parameters more uncertain. The values adopted are given in Table III; and the curves drawn in Figure 10 correspond to these values.

TABLE III

EFFECT OF OXIDATION ON RELAXATION CONSTANTS—STOCK F UNWORKED, 150% ELONGATION

	35°	70°	90.3°	113° C
		Vacuum		
α_s	0.00016	0.00017	0.00025	0.00028
α_t	0.00016	0.016	0.014	0.074
Relaxation time (days)				
Steady	2720	2560	1740	1550
Transient	2720	27	31	6
ζ_t	0.28	0.57	0.72	0.78
Heat of activation, kg. cal.				
Steady		1.7		
Transient		18.7		
		Air		
α_s	0.00010	0.0172	0.168	2.5
α_t	0.039	0.41		
Relaxation time (days)				
Steady	4343	25	2.6	0.17
Transient	11	1		
ζ_t	0.14	0.18	0.14	0.00
Heat of activation, kg. cal.				
Steady		30.9		
Transient		14.1		

ALTERNATIVE THEORIES OF RELAXATION

The assumption in the Tobolsky-Eyring theory that primary valence bonds in the vulcanized network can reform after being broken appears improbable, especially if we accept the conclusion that such breakage is due to oxidation. Tobolsky himself apparently has given up this assumption, if we may judge by his paper presented in this symposium; but no equations corresponding to such an alteration in the theory have been published. Consequently we present below such equations. In addition, we present a theory of transient relaxation involving a more detailed picture of the slippage process than has heretofore been used.

We adhere to the usual assumption that any relaxation phenomenon depends on a molecular process of bond rupture which is activated by thermal energy and may be accelerated by stress.

STEADY RELAXATION

We assume that the bonds ruptured in steady relaxation are primary valence bonds and that, once ruptured, they do not reform. At any given elongation, we may set the partial stress due to the primary bonded network as proportional to the number of unruptured molecular chains, assuming the force per unbroken chain to remain constant. That is:

$$f_s = f_{so}(N_s/N_{so}), \tag{19}$$

in which N_{so} = initial number of chains per unit cross-sectional area and N_s = number per unit area not yet broken.

The word chain in this connection means a section of chain molecule between vulcanized cross links.

According to this picture the stress per unruptured chain is f_{so}/N_{so}, and remains constant as the relaxation proceeds. If we assume the chains may be ruptured by combined thermal energy and stress, then:

$$\frac{dN_s}{dt} = -N_s\nu R_s \exp(-H_s/kT)\int_0^{\pi/2} \exp\left(\frac{\lambda f_{so}\cos\theta}{N_{so}kT}\right)\sin\theta d\theta \qquad (20)$$

$$= -N_s\nu R_s \exp(-H_s/kT)\frac{N_{so}kT}{\lambda f_{so}}\left[\exp\left(\frac{\lambda f_{so}}{N_{so}kT}\right) - 1\right]$$

where ν is the number of rupturable bonds per chain, R_s is a rate constant, H_s the heat of activation, λ is the relative displacement or increase in distance of two bonded molecules when bond rupture is complete, k is Boltzmann's constant, T is absolute temperature, and θ is the angle between the interatomic tension and the momentary direction of the relative thermal vibrations of the two molecules. R_s varies with temperature, but to an extent small compared with the exponential $\exp(-H_s/kT)$. In setting up the integral, it is assumed that all directions of relative thermal vibration are equally probable. In this equation f_{so} must always be a positive tension.

Integration of (20) with the initial condition $N_s(0) = N_{to}$ gives, with the aid of Equation (19):

$$f_s = f_{so}\exp\left[-t\nu R_s \exp\left(-\frac{H_s}{kT}\right)\frac{N_{so}kT}{\lambda f_{so}}\exp\left(\frac{\lambda f_{so}}{N_{so}kT}\right) - 1\right)\Bigg] \qquad (21)$$

It is to be observed that, while this equation states that the rate of steady relaxation increases with initial stress if $\lambda f_{so}/N_{so}kT$ is of the order 1 or greater, the dependence on stress is different from that indicated by the Tobolsky-Eyring Equation (7). According to Equation (21) the relative rate of stress relaxation, $-(1/f_s)(df_s/dt)$, is constant at any elongation but increases with elongation (or initial stress); while according to Equation (7) the rate initially is high for high elongations but approaches with time the rate for low elongation.

Equation (21) has been used in analyzing steady relaxation in the experiments reported. However, since Equations (21) and (7) differ in their dependence on observables only in the form of their sensitivity to stress, and since the experimental data themselves show so little sensitivity of steady relaxation to stress, the results of the analyses by the two equations are very little different.

TRANSIENT RELAXATION

We now proceed to an analysis of transient relaxation. In this case we introduce a picture of the transient mechanism which postulates longitudinal chain slippage to equalize the stress along the chain between two cross-linked points. According to this picture, transient relaxation consists of the repeated rupture of crystallites or other secondary bonds, accompanied by slippage of the chain molecules and reformation of the bond after the chain tension on the two sides of the bond or crystallite has been locally equalized. If there was no difference in tension before rupture, then the bond will reform without any chain slippage.

We shall make our mathematical analysis of this problem in reverse, so to speak; and we begin by considering a sample of elongated rubber in which the transient relaxation is complete. We suppose that a chain molecule, shown in Figure 14, is cross-linked at points A and B; and is attached to other molecules

at C by a bond having greater energy than the other bonds along AB. To be specific, we shall speak of C as a crystallite.

Starting with equal tension in chain-sections AC and CB, let the chain molecule be pulled through the crystal so that the chain point P is displaced the distance ϵ to point P'; while the crystal is displaced the distance δ, to point C'. In this configuration the point P'' on the chain is reattached and becomes part of the crystal. ϵ and δ are opposite in sign and so related that the resulting tension unbalance in the chain balances the elastic restoring force on the crystal. That is:

$$\mu\delta = -\epsilon\eta\left(\frac{1}{x_1}+\frac{1}{x_2}\right) \tag{22}$$

where μ = elastic force constant for the displaced crystal; η/x_1, η/x_2 = force constant for the stressed molecule in section AC, CB; and x_1, x_2 = length of section AC, CB.

The constant η takes into account both the elongation of the chain and the distortion of the chain path in regions of curvature. We have assumed here that points A and B are immovable. The dotted line in Figure 14 indi-

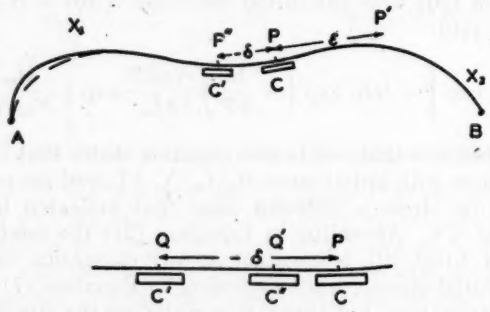

FIG. 14.—Transient relaxation by longitudinal molecular slippage. A, B are cross-linked points. C is a crystallite. After point P on the molecule is released from the crystallite, the crystallite jumps to position C', where attachment to point Q on the molecule occurs. In this attached state Q and C' subsequently move to the new equilibrium position $Q'C''$.

cates the nature of the path distortion caused by an increase in chain tension in section AC.

In this stressed state the increase in elastic energy in the system is:

$$\Delta E = N_c\left[\frac{\mu}{2}\delta^2+\frac{\eta}{2}\left(\frac{1}{x_1}+\frac{1}{x_2}\right)\epsilon^2\right] \tag{23}$$

N_c being the number of such displaced crystallites/cm.^{3}.

Now if ϵ and δ have the proper values, this complex state of deformation can be reached in a more regular procedure, namely, by instantaneously stretching the sample from zero to the given elongation. If the state thus attained is the same, Equation (23) applies equally to the situation developed by either procedure. The increment in stress on the sample due to the local deformations is obtained by differentiating (23) with respect to e, the elongation:

$$\Delta f = \frac{d\Delta E}{de} = N_c\left[\mu\delta\frac{d\delta}{de}+\eta\left(\frac{1}{x_1}+\frac{1}{x_2}\right)\epsilon\frac{d\epsilon}{de}\right] \tag{24}$$

Let us set

$$d\delta/de = p, \qquad d\epsilon/de = q \tag{25}$$

Since the stress equilibrium indicated by Equation (22) must still hold, we have:

$$\mu p = -\eta\left(\frac{1}{x_1}+\frac{1}{x_2}\right)q \tag{26}$$

By using Equations (22), (25), and (26), Equation (24) can be thrown into either of the equivalent forms:

$$\Delta f = N_c\mu p\delta\left[1+\frac{\mu}{\eta\left(\frac{1}{x_1}+\frac{1}{x_2}\right)}\right] \tag{27}$$

$$\Delta f = N_c\eta\left(\frac{1}{x_1}+\frac{1}{x_2}\right)q\epsilon\left[1+\frac{\eta}{\mu}\left(\frac{1}{x_1}+\frac{1}{x_2}\right)\right] \tag{28}$$

These two equations are valid for any values of δ and ϵ, p and q, subject to the conditions (22) and (26). We may, therefore, consider δ and ϵ as decreasing in magnitude with time, and identify Δf with f_t, the remaining transient stress. Therefore we may write:

$$\frac{f_t}{f_{to}} = \frac{\Delta f}{\Delta f_o} = \frac{\delta}{\delta_o} = \frac{\epsilon}{\epsilon_o} \tag{29}$$

We must now examine the problem of how δ or ϵ varies with time. If we assume that the chain molecule is so restricted that it can break loose from the crystal only in kinetic movement parallel to its direction in the crystal, we deduce that the probability of breaking loose is:

$$R_t \exp\left(-\frac{H_t}{kT}\right)\left[\exp\left(\frac{\lambda\mu\delta}{kT}\right)+\exp\left(-\frac{\lambda\mu\delta}{kT}\right)\right] = 2R_t\exp\left(-\frac{H_t}{kT}\right)\cosh\frac{\lambda\mu\delta}{kT} \tag{30}$$

where the different variables are defined as those in Equation (20). $\mu\delta$ is, by previous definitions, the force between chain and crystallite.

If we assume, on the other hand, that the chain is attached to the surface of the crystallite and is free to break away in any direction in the half-space lying outside the crystal, the probability of breaking loose takes a somewhat different form. Let us assume further, in this case, that the force tending to pull the chain loose lies parallel to the crystal surface. If θ is the angle between this force and the momentary direction of the thermal vibration of the attached chain segment relative to the crystallite, the probability of breaking loose is:

$$\int_0^\pi R_t\exp\left(-\frac{H_t}{kT}\right)\exp\left(\frac{\lambda\mu\delta\cos\theta}{kT}\right)\sin\theta d\theta = \frac{2R_tkT}{\lambda\mu\delta}\exp\left(-\frac{H_t}{kT}\right)\sinh\frac{\lambda\mu\delta}{kT} \tag{31}$$

It has been found that the two probability expressions (30) and (31) lead to expressions for relaxation which cannot easily be distinguished experimentally. Other reasonable assumptions regarding the mechanism of crystallite rupture would presumably lead to other probability expressions not greatly different from the above pair. On the basis of greater mathematical simplicity, we shall adopt the sinh function (31) in what follows.

Referring to the lower detailed drawing of Figure 14, we assume that when the chain at point P breaks loose from the crystallite C there is an instantaneous release of local stress, in that the crystallite jumps the distance δ and returns to C', its equilibrium position in the surrounding rubber. The chain, on the other hand, while momentarily free, relaxes much more slowly, because its complete relaxation involves a sequence of local slippages extending over the whole length of the chain between vulcanized cross links. The crystallite in position C' therefore reattaches the chain at a new point Q, which is separated from P by the distance δ. After reattachment, the chain and crystal gradually come to a new position of equilibrium, the crystal now being at C'' and the attached point Q at Q'. Since the net change in displacement of the chain relative to the crystal is δ, the average rate of change in this relative displacement is δ times the probability expression (31). Also, by definition of δ and ϵ, the relative displacement of chain and crystal, referred to their positions when the chain stress is equalized, is $\epsilon - \delta$. Therefore we have:

$$\frac{d(\epsilon - \delta)}{dt} = \frac{2R_t kT}{\lambda\mu} \exp\left(-\frac{H_t}{kT}\right) \sinh\frac{\lambda\mu\delta}{kT} \tag{32}$$

After eliminating ϵ by using Equation (22), we can integrate (27) and obtain:

$$\tanh\frac{\lambda\mu\delta}{2kT} = \tanh\frac{\lambda\mu\delta_o}{2kT} \exp\left[-\frac{2tR_t \exp\left(-\frac{H_t}{kT}\right)}{1 + \frac{\mu}{\eta\left(\frac{1}{x_1} + \frac{1}{x_2}\right)}}\right] \tag{33}$$

Substitution for δ from Eq. (29) now gives us:

$$\tanh\frac{\lambda\mu\delta_o f_t}{2kTf_{to}} = \tanh\frac{\lambda\mu\delta_o}{2kT} \exp\left[-\frac{2tR_t \exp\left(-\frac{H_t}{kT}\right)}{1 + \frac{\mu}{\eta\left(\frac{1}{x_1} + \frac{1}{x_2}\right)}}\right] \tag{34}$$

This equation is of the same form in f_t and t as the Tobolsky-Eyring Equation (8). Thus, the new equation is no better and no worse in fitting experimental data. There is considerable difference, however, in the interpretation of the parameters b_t and α_t.

GENERAL DISCUSSION

Although the data of these experiments cover a wide range in time, temperature, and elongation, it was nevertheless impossible to determine uniquely or with much accuracy the parameters in the theoretical equations; and it was

impossible to distinguish between the two different formulas for steady relaxation. It is obvious that the residuals, or transient relaxation, must be very sensitive to the curve assumed for steady relaxation.

Some such difficulty as this may be back of our value for the heat of activation of transient relaxation, 15 kg. cal., which seems rather high. However, if this value is correct, it may possibly be the sum of two components, one being the 10-kg. cal. involved in viscous shearing of raw rubber[4]; the other a 5-kg. cal. required to melt simultaneously 18 isoprene units out of a crystal, the latter figure being based on a heat of melting of 4 cal. per gram. Or, if viscous flow has nothing to do with the case, the 15-kg. cal. might be the heat of melting of 56 isoprene units from a crystal.

The heats of activation in vacuum, reported in Table III, are of doubtful validity, particularly the value of 1.7 kg. cal. for steady relaxation. Such a low value requires verification in an experiment in which the sample is degassed, or subjected to a vacuum for some time before being stretched.

There are small but systematic discrepancies between some of our theoretical curves and the experimental data for short times. These discrepancies are in such a direction as to indicate the existence of a third relaxation mechanism, of a higher relaxation rate than the rate of transient relaxation found in our analysis. Recent data[4] of Shore Durometer reading as a function of time after 0.1 second definitely establish such a high relaxation rate. In view of this fact and the fact that our data were found insufficient for a precise or unique determination of the parameters in our analysis, it appears that a complete analysis of relaxation will require more extensive data than have yet been published. Measurements should begin at 0.1 second or less after stretching, should extend to practically complete relaxation, and should cover the maximum possible range in elongation. To avoid termination of the test by rupture of the sample, tests should perhaps be made with shear or compression instead of elongation.

Further theoretical work is in progress, in which the theory of transient relaxation based on longitudinal molecular slippage is being extended. The extension consists of assuming such a large number of intermolecular bonds along a chain that the crowded points can be treated as a continuous line of attachment, with a constant energy of attachment per unit length along the molecule. The analysis, although not yet complete, has shown, as a necessary consequence of the theory, that there must be a large spread in relaxation rates arising from this one type of relaxation process.

GLOSSARY

a = constant
$b_i = \lambda_i/4N_ikT$
e = base of natural logarithms; elongation
f = stress
f_o = initial stress
g = acceleration of gravity
h = Planck's constant
i = subscript—any relaxation type
k = Boltzmann's gas constant
n = exponent; also frequency
n_i = number of points of slippage per cm.
o = subscript—zero time
$p = d\delta/de$

q = $d\epsilon/de$
r = subscript—rubber
s = subscript—steady
t = time; subscript—transient
w = subscript—wire
x = $10^{-\alpha_s t} \tanh \beta_s$; length of section
y_i = f_i/f_{io}
x_1, x_2 = length of chain segment from crystallite to cross-linked point
A = constant
B = constant
C = proportionality constant
D_m = drift with respect to deformation at 1 minute
ΔE = increment in elastic energy of system
$F(x)$ = function of x defined in Equation (17)
ΔF_i = free energy of activation of slippage of ith type
G_i = modulus of ith type
H_m = height at 1 min; H_t = height at time t; H_o = unloaded height
H = heat of activation of rupture
L = length
N_c = number of displaced crystallites per cc.
N_i = number of i type stress-bearing units per sq. cm.
N_s = number of chains per sq. cm. not broken
R = relative relaxation; also a rate constant
S = relative stress
T = tensile force; absolute temperature
Y = f/f_o
α_i = relaxation rate of ith type
β_i = $b_i f_{io}$
δ = displacement of crystal
ϵ = displacement of chain point
ζ_i = f_{io}/f_o
η = modulus of stress in sections AC and CB
μ = elastic force constant for displaced crystal
λ_i = distance jumped by unit of i type at each slip, projected onto direction of stress
λ = increase in distance of two bonded molecules when rupture is complete
ρ = linear density
τ = subscript—reference time or time of first reading
θ = angle between intermolecular tension and momentary direction of the relative thermal vibration
ν = number of rupturable bonds per chain

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HYSTERETIC AND ELASTIC PROPERTIES OF RUBBERLIKE MATERIALS UNDER DYNAMIC SHEAR STRESSES *

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The principal problem of the rubber technologist and engineer today is that of applying the various types of synthetic rubber to products which undergo rapid repeated flexure. All commercially available synthetic rubbers possess a greater hysteresis defect than does natural rubber. Hence, the task of designing a product such as a large truck tire, where heat development has been no small problem even with natural rubber, is much more difficult. Consequently, the accompanying problem of evaluating the hysteretic properties of rubberlike materials has assumed new importance.

REQUIREMENTS OF A HYSTERESIS TEST

While early attempts to evaluate the mechanical properties of rubber emphasized the characteristic of high extensibility, it is now recognized that other more directly applicable properties, such as elastic modulus and elastic reversibility under dynamic low strain conditions, must be measured to predict the serviceability of a rubber or rubber stock. The service conditions of some rubber products are quite easily analyzed. For example, a transmission belt generally operates under a condition of constant maximum dynamic strain independent of the modulus of the stock, the magnitude and frequency of which can be calculated; a solid tire experiences periodic cycles of the same maximum stress. A pneumatic tire, however, is a complex structure of rubber and fabric which is not easily analyzed as regards the nature and frequency of the deformations of its various elements. The thin layers of ply stock in the carcass sidewall of the tire deform essentially in cycles of constant strain controlled by the fabric structure which undergoes cycles of constant predetermined amplitude for a given inflation pressure, load, and speed. The outer regions of the tread, however, deform in cycles of constant maximum compressional stress upon which are superposed constant bending strain cycles, the latter becoming increasingly important as the tread base is approached.

Gehman, Jones, and Woodford[1] have shown that approximately 50 per cent of the heat development in a pneumatic tire tread may be attributed to cycles of constant maximum strain independent of the modulus of the stock, the other 50 per cent being due to cycles of constant maximum stress in which the deformations depend on the modulus. Their experimental method was straightforward and the results must be considered significant. Nevertheless, their technique did not permit consideration of the contribution of the heat generated in the carcass to the observed temperature rise of the tread. Hence, their conclusions must be considered as subject to amendment when methods

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permitting a more complete analysis are devised. In any event, it is clear that a laboratory hysteresis test should be capable of measuring either the constant maximum strain or the constant maximum stress type of hysteresis index, if it is to be generally useful in predicting heat development in various types of products. It should employ rather low strains and reasonably high frequencies (20 cycles per second or higher). It should be noted that the frequency of deformation in a tire under normal operating conditions may be estimated at several hundred cycles per second, if the time required for a tread button to reach its full deformation after making contact with the road is considered. The uncertainty of the correctness of this concept is, fortunately, not important from the evaluation standpoint, since the relative values of the dynamic properties of different stocks do not change appreciably in the range of frequencies 20–300 cycles per second.

CLASSIFICATION OF HYSTERESIS TEST METHODS

Because of the dependence of hysteresis on minimum strain and rate of strain, the classical measurement of the area of the hysteresis loop obtained with a low speed tensile machine has been largely abandoned. Impact hysteresis methods[2] employing a pendulum or falling ball apparatus have become very popular because of their experimental simplicity. However, the fact that impact resilience is a function both of internal friction (the hysteresis defect) and dynamic modulus has been overlooked in many instances. Free vibration methods have been employed also[3], but only in a few cases have their results been correctly interpreted[4]. Relatively low frequencies are employed in free vibration tests and thus the measured internal friction, which decreases with frequency, is large. Hence, it is necessary to apply correction terms in the calculations which are negligible at higher frequencies. Forced vibration testers in which resonance is purposely avoided, generally termed flexometers, have served a very useful purpose[5]. In most cases, flexometers operate under arbitrary conditions chosen to develop heat in a rubber sample which can be measured by the temperature rise. The choice of the conditions of static and dynamic stress and strain has been unfortunate in several instances, and results are sometimes misleading. A recently developed electrically-driven flexometer[6] is not subject to this criticism, yielding temperature rise results under either constant maximum strain or constant maximum stress conditions.

The requirements of low strain, high frequency, and ability to measure constant strain and constant stress hysteresis are also met by several types of forced resonance vibrators[7]. With this type of equipment, a mechanical circuit, consisting of a rubber sample of dynamic stiffness S, a vibrating mass M, and a periodic impressed force $F \cos \omega t$, is tuned to resonance at a given radian frequency ω by varying M. The dynamic modulus E may then be calculated from the frequency and the resonance mass M_0, and the internal friction or hysteresis defect η is obtained from the resonance amplitude and the magnitude of the impressed force. These quantities are usually defined by the familiar differential equation of vibration in the linear dimension x:

$$M \frac{d^2x}{dt^2} + \frac{\eta}{q} \frac{dx}{dt} + \frac{E}{q} x = F \cos \omega t \qquad (1)$$

where Hooke's law is assumed and the damping force is defined proportional to the velocity (viscous damping). The quantity q is a geometrical constant which is the ratio of the height y to load area A of the test-piece for simple

compressional vibrations, such as were employed by Gehman, Woodford, and Stambaugh[8]. These workers established with well-designed apparatus that the dynamic modulus E and the product $\omega\eta$ are nearly independent of frequency, in agreement with Kosten[9]. Their resonance vibrator was mounted on a soft sponge rubber pad, which prevented loss of vibrational energy to the table. Thus, they avoided errors which Naunton and Waring[14] probably introduced by bolting their apparatus directly to a heavy base-plate. Stambaugh[10] studied the effect of temperature on E and η.

All of these experimenters employed compressional vibrations. Thus, their values of E and η depended on the shape of the particular sample employed as well as on the static compression. It would be highly desirable, of course, to be able to measure values E and η independent of sample shape, *i.e.*, which do not change with variation in $q = y/A$. The use of simple shear vibrations should accomplish this purpose. Hence, a forced shear vibrator, described in this paper, was developed.

THEORY OF SHEAR VIBRATIONS

If the sample of Figure 1 of thickness y and area A is vibrated in simple shear by an impressed shear stress $\sigma_m e^{i\omega t}$ and Hooke's law is assumed for the

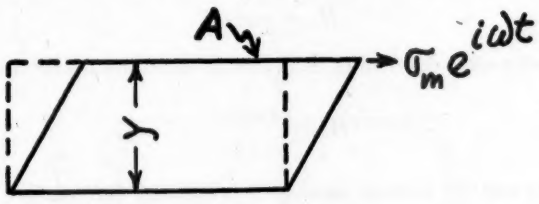

FIG. 1.—Simple shear diagram.

elastic restoring stress ($=G\epsilon$) and velocity damping for the viscous resisting stress ($=\eta\dot{\epsilon}$), the differential equation of vibration becomes:

$$qM\frac{d^2\epsilon}{dt^2} + \eta\frac{d\epsilon}{dt} + G\epsilon = \sigma_m e^{i\omega t}, \tag{2}$$

where ϵ is the instantaneous shear strain, G is the shear modulus, η is the internal friction, M is the mass of the vibrating system, and $q = y/A$. It should be noted that the internal friction η is defined as the viscosity of the sample and may be expressed in poises.

The steady state solution of (2) is:

$$\epsilon = \frac{\sigma_m}{[(G - qM\omega^2)^2 + \omega^2\eta^2]^{\frac{1}{2}}} e^{i(\omega t - \phi)}, \tag{3}$$

where the phase angle

$$\phi = \tan^{-1}\frac{\omega\eta}{G - qM\omega^2}.$$

For maximum amplitude (resonance)

$$G = qM_0\omega_0^2 - \eta^2/2qM_0, \tag{4}$$

where the subscript 0 indicates resonance values. In most actual materials

and for frequencies of 60 cycles per second or above, the term $\eta^2/2qM_0$ is very small and may be neglected. The maximum value of the resonance strain is then:

$$\epsilon_0 = \frac{\sigma_0}{\omega_0 \eta} \quad \text{and} \quad G = qM_0\omega_0^2. \tag{5}$$

Integration of the damping term $\eta\dot{\epsilon}$ over a full cycle gives the energy loss per cycle in unit volume:

$$H = \pi\omega\eta\epsilon_m^2 = \frac{\pi\omega\eta\sigma_m^2}{(G - qM\omega^2)^2 + \omega^2\eta^2} \tag{6}$$

which becomes at resonance:

$$H_0 = \pi\omega_0\eta\epsilon_0^2 = \frac{\pi\sigma_0^2}{\omega_0\eta}. \tag{7}$$

Now the resonance frequencies of the various elements of a tire are, in general, much greater than the impressed frequency $\omega/2\pi$. Hence, from (6) we obtain the hysteresis loss per cycle in unit volume, for those elements which respond in cycles of constant maximum strain:

$$H_\epsilon = \pi\omega\eta\epsilon_m^2 \tag{8}$$

and for those elements deforming in cycles of constant maximum stress,

$$H_\sigma = \frac{\pi\omega\eta\sigma_m^2}{G^2}. \tag{9}$$

Expressions (8) and (9) furnish means for predicting the relative heat development of various rubber stocks in the appropriate elements of a tire. Both expressions are nearly independent of frequency, since they depend on the quantities $\omega\eta$ and G. Formula (8) gives the heat developed in transmission belts; (9) gives that in a solid tire. The only limitation of their utility in predicting the temperatures developed in a pneumatic tire is the incomplete knowledge of the nature of the strain and stress cycles in the tread.

The foregoing analysis, based on the assumption that the damping stress is viscous in nature, as defined in (2), is far from satisfactory, for it has been shown that the internal friction η decreases with increasing frequency so that $\omega\eta$ is nearly constant. Thus, Equation (2) must be considered to hold only at a given frequency. This difficulty may be avoided by choosing the differential equation:

$$qM\frac{d^2\epsilon}{dt^2} + igG\epsilon + G\epsilon = \sigma_m e^{i\omega t}, \tag{10}$$

where g is a constant and $i = \sqrt{-1}$. The complex damping term is introduced on the assumption that the frictional stress is proportional to the elastic restoring stress $G\epsilon$ but is out of phase with it by an angle $\pi/2$. Since this assumption involves a frictional stress which is a maximum when the dynamic strain $\epsilon = 0$, the damping mechanism is sometimes considered analagous to a special type of solid friction. While this interpretation is somewhat forced, nevertheless, it is not unreasonable to picture the irreversible relative slippage of molecular elements as being associated with forces proportional to the dynamic strain but with minimum values at the extremes of relative slippage,

i.e., when the strain is a maximum. Without further attempts at interpretation, the steady state solution of (10) is found to be:

$$\epsilon = \frac{\sigma_m}{[(G - qM\omega^2)^2 + g^2G^2]^{\frac{1}{2}}} e^{i(\omega t - \phi)} \tag{11}$$

which is of the same form as (3). By comparison of (3) and (11), it is seen that:

$$g = \frac{\omega\eta}{G} \tag{12}$$

and, from the empirically known approximate frequency independence of $\omega\eta$ and G, g is seen to be a dimensionless constant which is nearly independent of frequency. The energy loss per cycle in unit volume is found to be:

$$H = \pi g G \epsilon_m^2 = \frac{\pi \sigma_m^2 \sin \phi}{[(G - qM\omega^2)^2 + g^2G^2]^{\frac{1}{2}}}. \tag{13}$$

Now, the dynamic hysteresis loop is an ellipse of area H. The ratio of the area of the loop to that of the circumscribing rectangle (see Figure 2) is some-

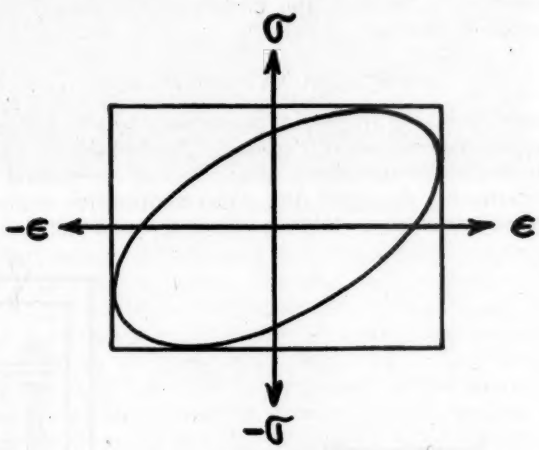

FIG. 2.—Dynamic hysteresis loop.

times referred to as the fractional or per cent damping:

$$h = \frac{\pi}{4} \frac{gG}{[(G - qM\omega^2)^2 + g^2G^2]^{\frac{1}{2}}} = \frac{\pi}{4} \sin \phi \tag{14}$$

which for the condition applying in a tire, $\omega \ll \omega_0$, becomes:

$$h' = \frac{\pi}{4} g. \tag{15}$$

The significance of the quantity g is not so clear as the name fractional damping suggests. The area of the rectangle circumscribing the elliptic hysteresis loop

represents 4× the product of the maximum dynamic stress by the maximum dynamic strain:

$$H_R = 4\epsilon_m\sigma_m = \frac{4\sigma_m^2}{[(G - qM\omega^2)^2 + g^2G^2]^{\frac{1}{2}}}. \qquad (16)$$

Thus, H_R is a rather artificial quantity where the phase angle ϕ is neglected but is not allowed to vanish, since, for $\phi = 0$, $g = 0$. Otherwise stated, H_R is 4× the vibrational energy stored in unit volume in a quarter-cycle and g is proportional to the ratio of energy absorbed to energy stored in a quarter-cycle, for the condition $\omega \ll \omega_0$. Since this condition $\omega \ll \omega_0$ also applies to the case of ordinary impressed mechanical frequencies as compared to the high natural frequencies of molecular segments, g has definite value as an index of the molecular hysteresis defect. In evaluating the relative hysteretic virtues of two stocks in a product, however, exactly the same results are obtained in calculating H_ϵ and H_σ, regardless of whether g or η is employed as the hysteresis defect. In fact, it is usually necessary to specify a value of G, from other considerations not involving hysteresis, and the use of η or $\omega\eta$ as a hysteresis index is somewhat more convenient than employing g, which is explicitly dependent on G. It must be remembered, of course, that both G and $\omega\eta$ (or g) are functions of temperature and, for their values to have significance in calculating heat development in a product, the measurements should be made in the temperature range of service.

APPARATUS AND TECHNIQUE

The resonance shear vibrator is shown schematically in Figure 3. A photograph of the apparatus is shown in Figure 4. The cylindrical rubber samples 0 are clamped between the stationary plates N and the central plate C. For most of the experiments described, the static compressive strain was 0.15 and the samples were cylinders of 4.05-cm. diameter and 1.90-cm. height. The

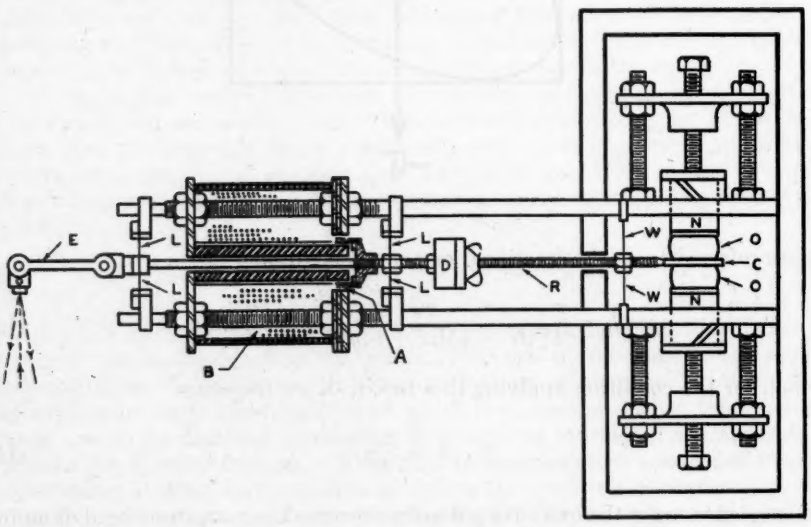

FIG. 3.—Schematic drawing of resonance shear vibrator.

central plate was attached rigidly to the brass rod R which was suspended by the light steel leaf springs L and steel wires W. The rod could be loaded with steel weights D so that the vibrating mass of the system could be varied from 317 to 6317 grams. The samples were vibrated in shear at right angles to their static compression when alternating current was passed through the coil A, which was suspended in the electromagnetic field of the loudspeaker field coil B. The moving coil A consisted of 54 turns of No. 24 B. and S. enameled copper wire wound on a 3.47-cm. diameter paper core. The coil and core were impregnated with Bakelite varnish and baked to give a light rigid unit.

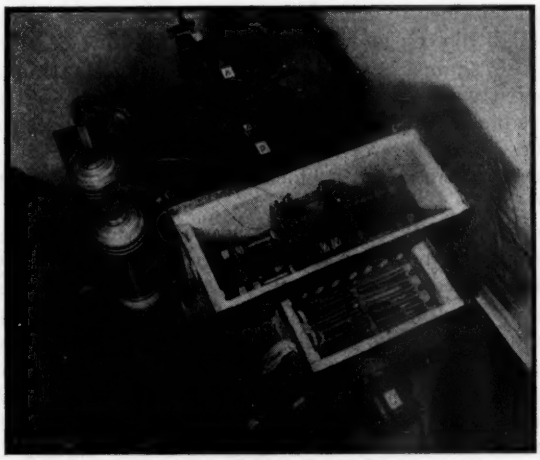

FIG. 4.—Resonance shear vibrator.

The direct current voltage for the field coil B was furnished by a power pack connected to the output of a voltage regulator. Alternating current was supplied to the moving coil either from the 60-cycle mains through an auto transformer or from a 100-watt amplifier-oscillator unit, the frequency of which could be varied from 20 to 20,000 cycles per second. The output impedance of the amplifier was matched with the impedance of the moving coil, and the sinusoidal character of the current in the coil was confirmed frequently by means of a cathode-ray oscillograph. The shear force-current characteristic was determined by loading the rod R horizontally with dead weights suspended by a cord over a pulley and balancing the known mechanical force against the force exerted by a direct current in the coil. The force-current relationship was accurately linear. The amplitude of vibration was measured by an optical lever system with an amplification factor of 115. The light source was a 6–8-volt headlight bulb which was supplied with 8 volts a.c. Light from the bulb was reflected to the transparent scale by means of the pivoted, moving concave mirror F actuated through the connecting rod E. Thus, a continuous illuminated line appeared on the scale, the length of which was 230× the amplitude of vibration. For measurements of static modulus, where a direct current was passed through the moving coil, the static deflection was measured by the displacement of the spot of light on the scale 10 seconds after application of the current. In practice, the average of the positive and negative deflections, obtained by reversing the current, was taken as the static deflection.

The rubber samples were enclosed in a Marinite box, which could be maintained at elevated temperature by means of heated air or at lower temperatures by injecting expanding CO_2 gas. The temperature of the box was controlled by means of a thermocouple junction at the center of one of the samples activating a potentiometer recorder-controller for one-half the control cycle and by a junction in the air stream immediately adjacent to the sample for the other half of the cycle. This method of control required a much shorter time to reach thermal equilibrium than was needed by control from a junction in the air stream alone (15 minutes instead of 45 minutes to reach 100° C). Furthermore, the dual control method gave a smaller temperature gradient in the sample than that obtained by control from the center of the sample alone (6° C instead of 12° C at 100° C) and less variation with time at any one point in the sample (± 1° C against ± 6° C). The junction in the rubber sample was accurately inserted with the iron and constantan wires lying parallel to the shear stress to reduce relative motion of the wires with respect to the adjacent layers of rubber. The vibrator was rigidly attached to a 200-kg iron press platen, which was supported on a block of latex sponge in order to minimize transmission of energy to the floor.

The system was usually tuned to resonance by varying the mass M until a maximum amplitude was obtained at a given driving current (given maximum stress σ_m). This procedure was greatly simplified by making a preliminary tuning by varying the frequency so that the approximate resonance mass at the desired frequency could be calculated. The values of the resonance mass M_0 and maximum amplitude X_0 were recorded. The maximum shear strain ϵ_0 was then calculated as X_0/y and values of G, $\omega\eta$, and g were determined from Equations (5) and (12). The values of H_ϵ and H_σ relative to those obtained with a standard Hevea rubber tread stock at 50° C (setting $H_\epsilon = 100$ and $H_\sigma = 100$ for the standard stock) were calculated by means of Equations (8) and (9). In most cases, measurements were made at a frequency of 60 cycles per second at temperatures of 50° C and 100° C.

For special experiments, the resonance stress, as determined by the driving current, was measured at constant amplitude. Other experiments included the measurement of the dynamic properties with varying frequency, static compressive strain, dynamic strain, sample dimensions, and temperature.

PREPARATION OF TEST-SPECIMENS

The formulation (parts by weight) of the various stocks employed in this investigation is given in Table I. The low black stocks were compounded to possess properties permitting measurements over a wide range of static compressive strains. The gum type stocks were compounded as simply as possible to permit direct comparisons of the various base rubbers without introducing the reinforcing effect of carbon black. The tread type stocks were compounded with the same weight loading of black and with as few other variations as were consistent with satisfactory mixing and vulcanizing characteristics. Stocks employed in the study of the physical parameters were mixed on a laboratory mill. The GR-S was obtained from a factory batch. Stocks for the study of chemical parameters were mixed in a small Banbury. The GR-S in this case was polymerized in a laboratory autoclave. Different lots of Hevea rubber were employed in the two studies. Thus it was to be expected that the absolute values of the physical properties might differ in the two cases. As an

TABLE I

STOCK FORMULATION

Pigment	Low black		Gum type					Tread type				
	Hevea	GR-S	Hevea	Buna-S*	Butaprene -NM	Neoprene -GN	GR-I†	Hevea	Buna-S*	Butaprene -NM	Neoprene -GN	GR-I†
Polymer	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	3	2	3	2	2.5	—	2	3	2	3	—	2
Zinc oxide	5	5	3	5	5	5	5	3	5	5	5	5
Stearic acid	3	3	0.5	0.5	1	0.5	1.5	3.5	3	3	0.5	3
Captax	0.75	—	1	1.5	1.5	—	0.5	1	1.5	1.5	—	0.5
Santocure	—	1.2	—	—	—	—	—	—	—	—	—	—
Tuads	—	—	—	—	—	—	1	—	—	—	—	1
Agerite powder	1	—	1	—	—	1	—	1	—	—	1	—
Pine tar	—	3	—	—	—	—	—	3	—	—	—	—
Bardol	—	3	—	—	—	—	—	—	5	—	—	—
Dibutyl phthalate	—	—	—	—	—	—	—	—	—	20	—	—
Cottonseed oil	—	—	—	—	—	2.5	—	—	—	—	2.5	—
Calcined light magnesia	—	—	—	—	—	4.0	—	—	—	—	4.0	—
Altax	—	—	—	—	—	0.75	—	—	—	—	0.75	—
Pip-pip	—	—	—	—	—	0.5	—	—	—	—	0.5	—
Channel black	19.0	18.8	—	—	—	—	—	50	50	50	50	50

* This formulation was used for stocks of all butadiene-styrene ratios (including GR-S, 75/25).
† Butyl.

examination of the data will show, these differences did occur, particularly in the tread type stocks.

The stocks were cured in a press in a 3-piece cylindrical-cavity mould. The cures employed (see Table II) were selected as those corresponding to optimum values of tensile strength, measured with dumbbell samples in the conventional Scott testing machine. The cylindrical cured samples were buffed to within

TABLE II

CURING TIME AND TEMPERATURE

Stock	Curing time in minutes at 270° F		
	Gum type	Tread type	Low black
Hevea	75	75	65
Polybutadiene	100	100	—
Buna-S 85/15	100	100	—
Buna-S 75/25 (GR-S)	100	125	80
Buna-S 60/40	100	100	—
Butaprene-NM	75	100	—
Neoprene -GN	100	100	—
	Curing time in minutes at 300° F		
Butyl	75	100	—

±0.013 cm. (0.005 in.) of the desired height by means of a precision buffing jig. The effect of cure on dynamic modulus G and the hysteresis index $\omega\eta$ of Hevea and GR-S gum and tread stocks is shown in Table III. These stocks were mixed in a manner similar to those of the physical parameter studies.

EFFECTS OF VARIATIONS IN PHYSICAL PARAMETERS

The variation of dynamic modulus G with static compressive strain for the low carbon black stocks of Hevea and GR-S (see Table I) is shown in Figure 5. The decrease of G with increasing static compressive strain is approximately linear in the range studied. Likewise, in Figure 6, the hysteresis index $\omega\eta$ decreases nearly linearly with increasing static compressive strain. It should be remarked that the data for zero static strain were obtained with the rubber

TABLE III

EFFECT OF CURE ON DYNAMIC PROPERTIES (100° C TEST TEMPERATURE)

Stock	Cure at 270° F (132.2° C) (min.)	G Megadynes per sq. cm.	$\omega\eta$ Megagrams per cm. per sec.^{2}	θ	Ball rebound (%)
Hevea gum	25	3.22	0.114	0.0354	89.5
	50	3.22	0.104	0.0323	89
	75	3.30	0.115	0.0348	89
	100	3.14	0.135	0.0430	87
	125	3.06	0.151	0.0494	86.5
GR-S gum	50	4.17	0.392	0.0940	77
	75	4.11	0.392	0.0955	76.5
	100	4.31	0.403	0.0935	76
	125	4.09	0.415	0.1015	75
	150	4.03	0.407	0.1010	75
Hevea tread	25	11.48	2.11	0.184	54
	50	17.4	2.04	0.117	60
	75	17.8	1.85	0.104	62
	100	19.72	1.86	0.0944	62
	125	19.35	1.89	0.0978	62
	150	19.17	1.93	0.1006	61
GR-S tread	50	14.8	3.29	0.222	40
	75	15.3	3.16	0.206	44.5
	100	16.1	3.05	0.190	47
	125	18.3	3.09	0.169	48
	150	19.5	3.12	0.160	49
	175	19.18	3.12	0.163	50

samples cemented to the platens. Cementing was not necessary for static strains of 0.05 and greater, no slippage being observed. The curves of Figures 5 and 6 indicate no particular reason for selecting a standard static strain of 0.15, but considerations of experimental precision indicated this to be a practical choice.

The dynamic modulus G of Hevea and GR-S gum and tread stocks is seen to be independent of frequency in the range 25 to 180 cycles per second (see Figures 7 and 8), in agreement with the results of Gehman, Woodford, and Stambaugh[8]. A moderate increase in $\omega\eta$ with frequency for gum stocks is shown in the curves of Figure 9 and for the GR-S tread stock at 100° C in

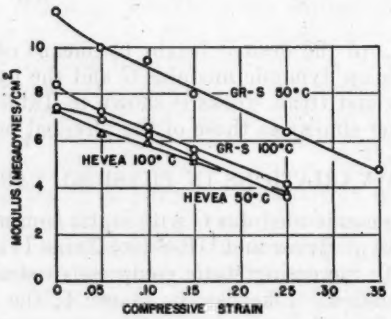

FIG. 5.—Dynamic modulus *vs.* static compressive strain in low black stocks; maximum impressed stress: 34,500 dynes per sq. cm.; frequency: 60 cycles per second.

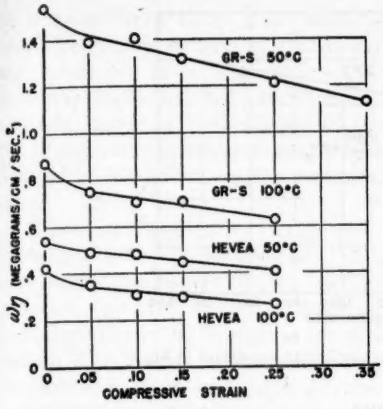

FIG. 6.—$\omega\eta$ *vs.* static compressive strain in low black stocks; maximum impressed stress: 34,500 dynes per sq. cm.; frequency: 60 cycles per second.

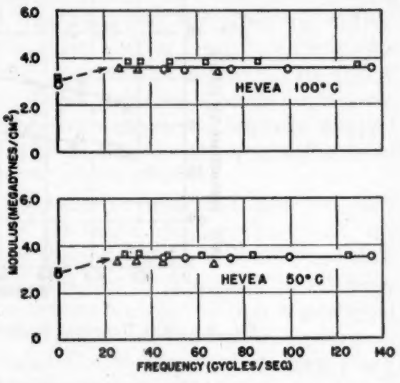

FIG. 7.—Dynamic modulus *vs.* frequency of Hevea gum stock; sample of constant area (14.2 cm.²) and varying thickness (0.228 cm. ⊙; 0.610 cm. ⊡; 1.88 cm. △); maximum impressed stress: 13,600 dynes/cm.²; static modulus at 10 seconds.

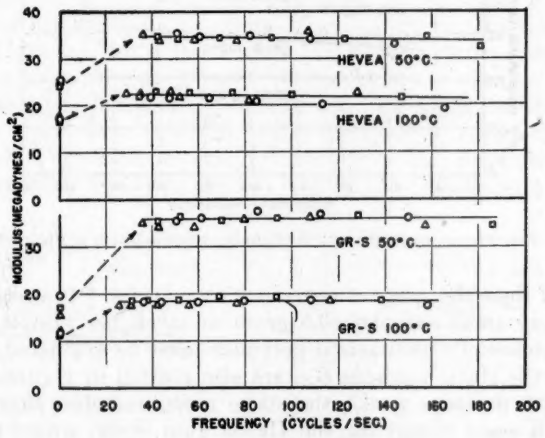

FIG. 8.—Dynamic modulus *vs.* frequency of tread stocks; samples of constant thickness (1.618 cm.) and varying areas (28.4 cm.² ⊙; 20.3 cm.² ⊡; 14.5 cm.² △); maximum impressed stress: 34,500 dynes per cm.²; static modulus at 10 seconds.

Figure 10. For the GR-S tread stock at 50° C and the Hevea tread at both 50° and 100° C, $\omega\eta$ is nearly independent of frequency. As indicated in Figures 9 and 10, several widely different sample shapes were employed in these experiments, different types of points being employed for the different sample shapes. Considering these curves as a group, no persistent trends in measured values of either G or $\omega\eta$ which can be attributed to sample shape appear. Considerably more scattering of the points occurs with the GR-S stocks than with the Hevea stocks, possibly because the GR-S stocks show a slight amount of permanent compressive set in the period required for a test. This independence of G and $\omega\eta$ of sample shape obtainable with the shear type test is highly desirable, since it permits extension of the experiments over wider ranges of frequency than can be attained with a given shape where the maximum and minimum values

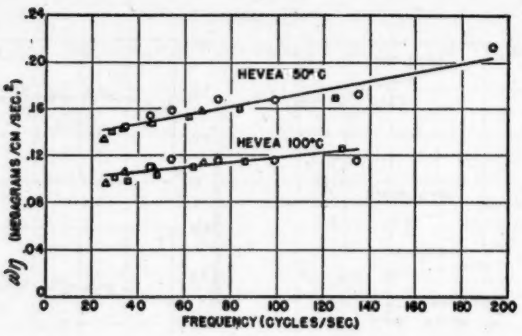

FIG. 9.—$\omega\eta$ *vs.* frequency of Hevea gum stock: test conditions of Fig. 7.

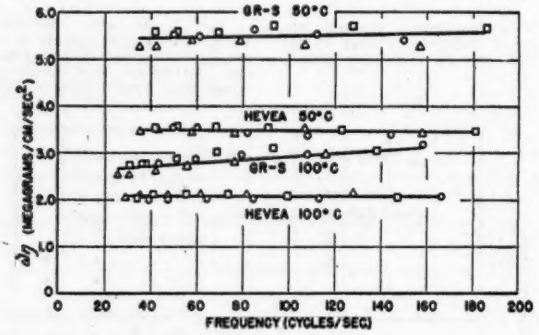

FIG. 10.—$\omega\eta$ *vs.* frequency; tread stocks; test conditions of Figure 8.

of the mass M limit the range of resonance frequencies. It also makes possible the use of very small samples (0.5 gram of stock per sample) where small laboratory batches of experimental polymers must be evaluated.

Values of the static modulus G_{St} are also plotted in Figures 7 and 8. In agreement with previous work[8], the static modulus is less than the dynamic modulus in all cases except for the Hevea gum stock, where the static and dynamic values are nearly the same. There seems to be only a slight possibility of a discontinuity in G between 0 and 20 cycles per second, but an investigation of G as a function of frequency in this range would be of considerable interest.

An investigation of the effect of rate of application of the load upon the static modulus G_{St} of GR-S tread stock at 100° C yielded rather interesting data, as follows:

Time required for application of 0.0345 megadynes/cm.² stress	Time of observation after application of stress	Observed "modulus" (megadynes/cm.²)
instantaneous	1 sec.	9.03
instantaneous	5	7.58
instantaneous	10	7.20
instantaneous	20	7.20
10 sec.	0	7.75
10 sec.	10	7.20

Dynamic modulus @ 60 cycles per sec. = 11.88.

It is clear from these data that the standard 10-second observation period employed in determining static modulus was adequate for attaining a true static value. It is also interesting to note that the measured value of the modulus increased with decreasing time of observation, between 10 and 1 seconds, possibly indicating the transition from static to dynamic modulus. No change in static modulus appeared when the stress was gradually applied instead of instantaneously, providing the time of observation was sufficiently large.

Since G is independent of frequency in the range investigated, the molecular hysteresis defect g varies with frequency in the same manner as $\omega\eta$ and, for that reason, no curves of g *vs.* frequency have been plotted. It should be borne in mind, however, that g is not entirely independent of frequency in all cases and Equation (10) is not as general as might be desired. From a practical testing standpoint, the independence of G and slight dependence of $\omega\eta$ or g on frequency is very fortunate, for it eliminates the necessity of making stock comparisons at tire frequencies, tests at frequencies of 20 cycles per second giving about the same relative values of G, $\omega\eta$, and g as at 200 cycles per second. It is desirable, of course, to make tests at a given frequency rather than with a given mass or moment of inertia, as is often done with free vibration apparatus.

Stambaugh[10], using compressional vibrations, found slight if any effect of amplitude on either the dynamic modulus or the internal friction of a Hevea gum stock. However, for a tread stock, he found a large decrease in both quantities with increasing amplitude. With the shear vibrator employed in this work a much smaller decrease of G and a very slight increase of $\omega\eta$ with dynamic shear strain were observed. The variation of G with dynamic shear strain ϵ for tread stocks is shown in Figure 11. The dependence of $\omega\eta$ on dynamic strain is shown in Figure 12. Stambaugh's data on a Hevea tread

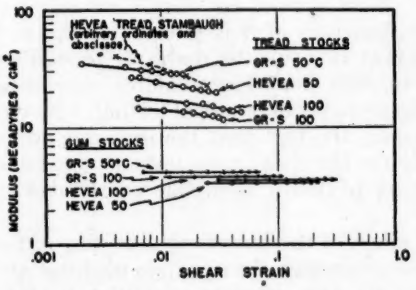

FIG. 11.—Dynamic modulus *vs.* dynamic shear strain; frequency: 60 cycles per second.

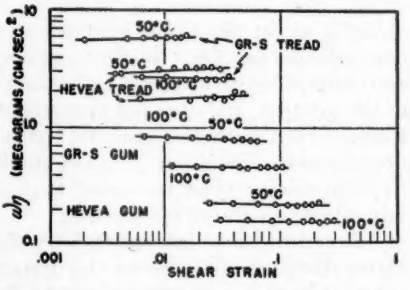

FIG. 12.—$\omega\eta$ *vs.* dynamic shear strain; test conditions of Figure 11.

type stock very similar to that of Table I are plotted with modulus and strain in arbitrary units for comparison in Figure 11. The markedly greater decrease of modulus with dynamic strain observed by Stambaugh for tread type stocks is not easily explained in the light of the independence of modulus on dynamic strain for gum type stocks. Any explanation based on a purely geometric factor such as the nature of the strain system in the sample appears untenable, since it would require approximately the same amplitude dependence for all types of stocks, within the limits of similarity of their stress-strain curves. It must be remembered, of course, that the static modulus decreases with increasing static strain in the low strain region of the stress-strain curve. Hence, the

slope of the major axis of the elliptic hysteresis loop, measured with respect to the strain axis, decreases with increasing maximum dynamic shear strain. The dynamic modulus, however, is not simply related to the ratio of dynamic stress to dynamic strain [see Equation (3)]. Hence, it appears that an understanding of the G *vs.* ϵ relationship demands knowledge based on a precise determination of the elliptic hysteresis loop, data on which are not now available.

Since the measurements of Figures 10 and 11 were made with a static compressive strain, normal to the dynamic shear strain, the static stress system in the sample was not as simple as would be desired. To investigate the effect of this nonuniform static strain distribution, measurements were made over a range of dynamic shear strains on a sample under zero compressive strain. These results are compared against those obtained with the same tread stock under 0.15 compressive strain in Figure 13. The dynamic strain dependence

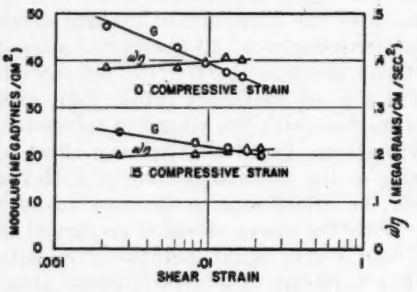

FIG. 13.—Effect of static compressive strain on the dynamic modulus and $\omega\eta$ *vs.* dynamic shear strain relationships; Hevea tread stock at 100° C; frequency 60 cycles per second.

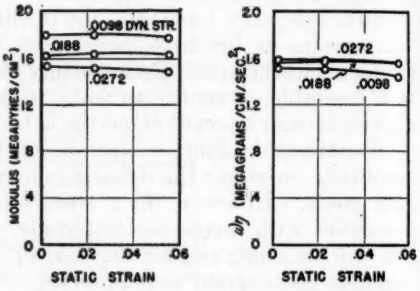

FIG. 14.—Effect on dynamic properties of imposing static shear strains upon the sample being tested under various dynamic shear strains; Hevea tread stock at 100° C.

of $\omega\eta$ is about the same for both cases, but that of G is greater for the zero compression sample. It thus appears that it would be desirable to employ zero compressive strain. Unfortunately, this procedure requires cementing of the samples, and does not meet the requirements of practical testing. Nevertheless, even with the samples compressed, the fact that the dynamic strain dependence of modulus is much smaller for the shear type tests as compared to compression type tests and that of $\omega\eta$ is almost negliglble constitutes an advantage for the shear method.

To obtain some information on the effect of the known nonlinearity of the static stress-strain curve on the dynamic properties, the dynamic modulus and internal friction were determined at three dynamic shear strains in the standard manner, but with three different static shear strains superimposed on the system by means of a spring whose natural resonance frequency was far from that of the vibrating system. The results are shown in Figure 14, where G and $\omega\eta$ are plotted against the static strain for three values of dynamic strain. It is seen that a change in static strain had very little effect on the dynamic modulus, whereas an increase in dynamic strain produced a decrease in modulus similar to that shown in Figure 11. The hysteresis index $\omega\eta$ also remained substantially unaffected with change in static strain and, as in the data of Figure 12, increased slightly with increase in dynamic strain. These data indicate that at least the major portion of the observed decrease in modulus with increase in dynamic strain is not explained by a nonlinearity in the static stress-strain curve since, for a given dynamic strain, a shift in the mean position

of the oscillation along the stress-strain curve resulted in almost no change in the dynamic modulus or $\omega\eta$.

Stambaugh[10] and Gehman[11] have remarked that dynamic modulus and internal friction appear to be linearly related when pigment loading and shape factor are varied. Stambaugh[10] suggests that the two indices are, therefore, simply related. The dissimilarity of the G *vs.* ϵ and $\omega\eta$ *vs.* ϵ curves of Figures 11 and 12 appears to contradict Stambaugh's conclusion.

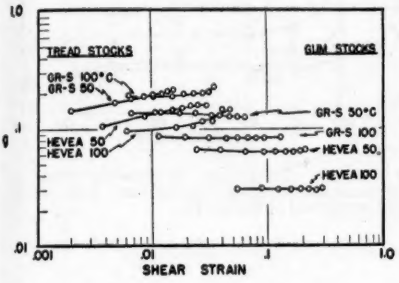

FIG. 15.—Molecular hysteresis defect *vs.* dynamic shear strain; test conditions of Figure 11.

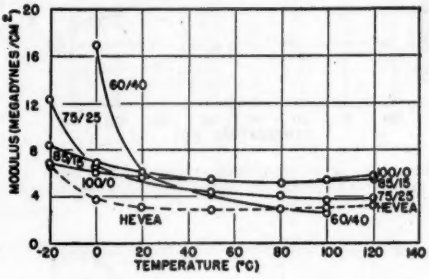

FIG. 16.—Dynamic modulus *vs.* temperature; butadiene-styrene ratio, gum stocks; maximum impressed stress: 34,500 dynes per sq. cm.; frequency: 60 cycles per second.

The relationship between g and ϵ is shown in Figure 15. The increase of g with ϵ for tread type stocks constitutes another departure from generality of Equation (10).

VARIATIONS IN SOME CHEMICAL PARAMETERS

As an example of the application of the forced shear vibrator, a rather complete study of the effect of variation of the butadiene/styrene ration on the dynamic properties of Buna-S type rubbers is presented in the curves of Figures 16 to 25. The Buna-S type polymers with differing butadiene/styrene ($=B/S$)

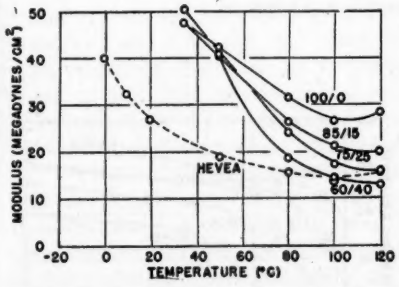

FIG. 17.—Dynamic modulus *vs.* temperature; butadiene-styrene ratio, tread stocks; test conditions of Figure 16.

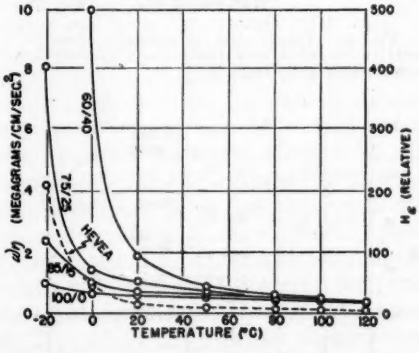

FIG. 18.—$\omega\eta$ *vs.* temperature; butadiene-styrene ratio, gum stocks; test conditions of Figure 16.

loading ratios, 60/40, 75/25, 85/15, and 100/0, were prepared by a uniform emulsion-polymerization process in a laboratory autoclave. Two stocks of each of the polymers were compounded in accordance with the gum type and

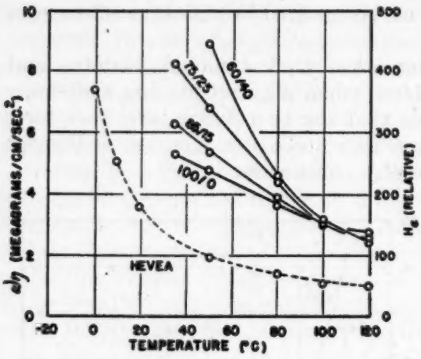

FIG. 19.—$\omega\eta$ *vs.* temperature; butadiene-styrene ratio, tread stocks; test conditions of Figure 16.

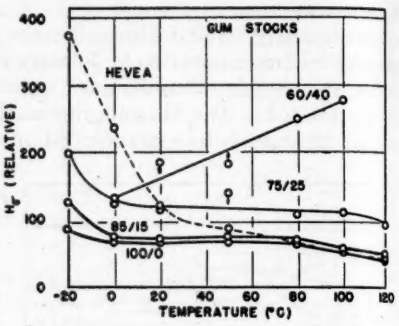

FIG. 20.—Energy loss at constant stress *vs.* temperature; butadiene-styrene ratio, gum stocks; test conditions of Figure 16.

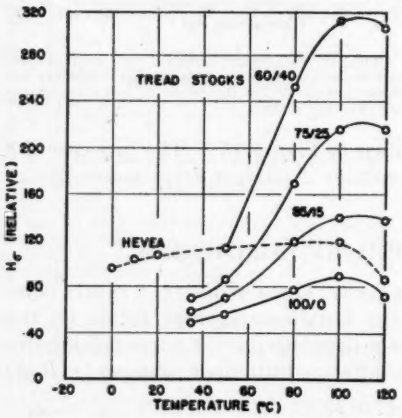

FIG. 21.—Energy loss at constant stress *vs.* temperature; butadiene-styrene ratio, tread stocks; test conditions of Figure 16.

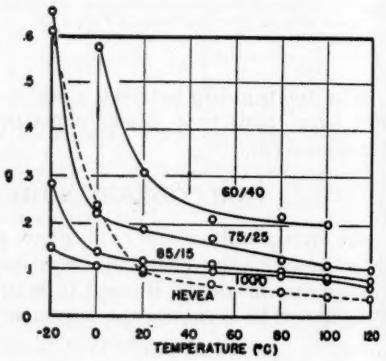

FIG. 22.—Molecular hysteresis defect *vs.* temperature; butadiene-styrene ratio, gum stocks; test conditions of Figure 16.

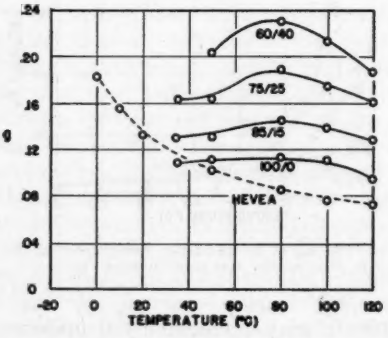

FIG. 23.—Molecular hysteresis defect *vs.* temperature; butadiene-styrene ratio, tread stocks; test conditions of Figure 16.

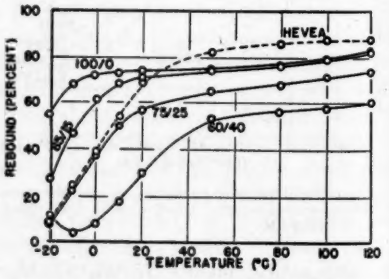

FIG. 24.—Ball rebound *vs.* temperature; butadiene-styrene ratio, gum stocks.

the tread type Buna-S formulation of Table I. All these measurements were made under conditions of 0.15 static compressive strain, 34,000 dynes per sq. cm. maximum stress, a frequency of 60 cycles per second, and with samples of 4.05-cm. diameter and 1.90-cm. height. The various properties are represented as functions of temperature. Curves for comparably compounded

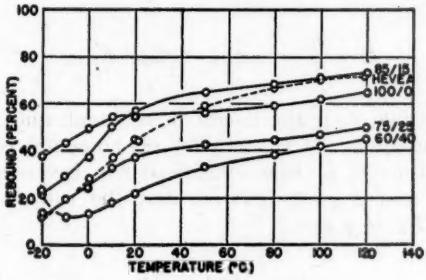

FIG. 25.—Ball rebound *vs.* temperature; butadiene-styrene ratio, tread stocks.

Hevea rubber gum and tread type stocks are included for reference (see Table I for formulation).

The temperature coefficients of G and $\omega\eta$ decrease with increasing butadiene/styrene ratio for both gum and tread stocks (see Figures 16 to 19). Distinct cross-overs are found in the G *vs.* temperature curves (Figures 16 and 17), indicating that Buna-S with a high butadiene content has superior elastic properties for low temperature service. This conclusion is in agreement with the work of Liska[12] on static modulus at low temperature. At the higher temperatures the order of the curves for the various B/S ratios is the same for both gum and tread stocks. The slope of the curves for the Buna-S tread stocks in the intermediate temperature region is much greater than for the gum stocks and for the Heavea tread stock. It is of interest to note that Buna-S (75/25) has nearly the same modulus G as Hevea rubber at 120° C, which is in the range of truck tire operating temperatures. The hysteresis index $\omega\eta$, however, is much higher for all the Buna-S type polymers than for Hevea, both in gum and tread formulae. The relative heat generation at constant maximum strain H_ϵ, of course, varies in exactly the same manner as $\omega\eta$, and its values are indicated in Figures 18 and 19. Since the differences in $\omega\eta$ for the various Buna-S type polymers disappear as the temperature increases, any differences in the index g, ball rebound, or H_σ at elevated temperatures must result from the differing values of G. As might be expected, the molecular hysteresis defect g shows smaller temperature coefficients than are found in $\omega\eta$ (see Figures 22 and 23). The heat generation at constant maximum stress H_σ shows positive temperature coefficients for the 60/40 polymer in the gum formula and for all the Buna-S type polymers in the tread formula. In general, increasing the butadiene content appears to yield a polymer which approaches Hevea with respect to the hysteretic properties $\omega\eta$, g, H_ϵ, and H_σ in their temperature dependences. This is not true in regard to the modulus G or other properties not considered in this paper.

The impact resilience, determined by the rebound of a falling ball or a pendulum hammer, has been employed extensively by rubber technologists as a measurement of hysteresis. Hence, it is of interest to compare results of rebound measurements with forced vibrator data. Impact resilience was de-

termined as the per cent rebound of a 1.9-cm. diameter steel ball bearing falling from a height of 1 meter upon the flat surface of a rubber cylinder (4.05-cm. diam., 1.90-cm. height), held against a heavy horizontal plate by vacuum applied through small drilled holes in the plate. Per cent resilience is plotted against temperature in Figures 24 and 25. Simple energy considerations based on the theory of free vibration show that the fractional impact resilience may be expressed as:

$$R = \frac{h_2}{h_1} = \exp\left(-\pi\omega_0\eta/E_R\right), \tag{17}$$

where h_1 is height of fall, h_2 is the height of rebound, and E_R is the effective dynamic Young's modulus. If the impact phenomenon is considered as involving a single half-cycle of free vibration, the frequency and amplitude dependences of $\omega_0\eta$ and E_R are ignored, and the rubber is assumed to be incompressible; $\omega_0\eta/E_R = g$ and

$$g = \frac{1}{\pi}\ln\left(\frac{1}{R}\right). \tag{18}$$

Values of g calculated from ball rebound data by Equation (18) and from forced vibrator data are given in Table IV. The rebound values of g are consistently

TABLE IV

COMPARISON OF VALUES OF g OBTAINED BY MEANS OF REBOUND AND FORCED VIBRATION (TREAD STOCKS)

Temperature (° C)	Property	Hevea	Buna-S type rubbers 60/40	75/25	85/15	100/0
50	g by rebound	0.168	0.347	0.235	0.214	0.182
50	g by forced vibration	0.100	0.215	0.164	0.132	0.112
100	g by rebound	0.112	0.276	0.240	0.193	0.152
100	g by forced vibration	0.077	0.213	0.174	0.139	0.110

Rebound: $g = (1/\pi) \times 2.30 \times \log_{10}(1/R)$.
Forced vibrator: $g = \omega\eta/G$.

higher, indicating that the assumptions leading to Equation (18) are too simple. Nevertheless, the relative values of g for different rubbers and temperatures, as determined by the two methods, agree surprisingly well. Thus, the impact type of test may be considered as a simple method of obtaining relative values of g. With pendulum type impact apparatus it is possible to measure the dynamic deflection of the hammer as well as the resilience, and thus a quantity corresponding to dynamic modulus may be calculated. It should be emphasized, however, that falling ball or pendulum resilience alone is a measure neither of H_ϵ or H_σ, the principal heat generation indices.

The results of another experiment in which five commercial rubbers; Hevea, GR-S, Butaprene -NM, Neoprene-GN, and GR-I, were compared are given in Table V. The comparison was made both in gum and tread-type formulae at three temperatures. The temperature coefficients of the various indices vary greatly between the different rubbers. Neoprene-GN has much the lowest temperature coefficients for G and $\omega\eta$ in both the gum and tread formulas, in the temperature range 30° to 100° C. Thus, the superiority (low $\omega\eta$ and H_ϵ) which it shows over the other synthetics at room temperature disappears at

TABLE V

DYNAMIC PROPERTIES OF VARIOUS RUBBERS. MAXIMUM DRIVING SHEAR STRESS = 34,500 DYNES PER SQ. CM.; FREQUENCY = 60 CYCLES PER SECOND; STATIC COMPRESSIVE STRAIN = 0.15

Stock type	Base rubber	$\omega\eta(\alpha He)$ (megagrams/cm./sec.²)			G' (megadynes/cm.²)			G_{st} (megadynes/cm.²)			g (dimensionless)			He (relative to Hevea tread at 50° C)		
		30° C	50° C	100° C	30° C	50° C	100° C	30° C	50° C	100° C	30° C	50° C	100° C	30° C	50° C	100° C
Gum	Hevea	0.270	0.205	0.132	3.08	2.97	3.09	2.53	2.56	2.72	0.088	0.080	0.043	533	450	266
	GR-S	0.958	0.734	0.417	5.29	4.43	3.74	2.67	2.56	2.72	0.181	0.165	0.111	642	720	573
	Butaprene-NM	2.295	1.048	0.696	9.43	7.92	6.86	4.82	4.23	4.98	0.243	0.132	0.101	459	320	284
	Neoprene-GN	1.01	0.700	0.682	6.21	5.24	4.59	3.31	2.61	2.20	0.163	0.134	0.149	496	496	620
	GR-I	2.49	0.765	0.250	4.11	3.17	2.56	2.29	2.21	2.21	0.607	0.241	0.113	2390	1430	718
Tread	Hevea	3.02	1.92	1.07	24.0	19.2	13.9	17.9	17.1	12.8	0.126	0.100	0.077	95	100	106
	GR-S	8.76	6.74	3.04	53.8	41.1	17.4	25.1	18.3	9.9	0.163	0.164	0.174	56	76	191
	Butaprene-NM	5.10	3.06	1.48	27.3	20.1	13.2	14.6	11.6	9.9	0.187	0.144	0.112	126	132	162
	Neoprene-GN	5.00	2.78	2.02	26.5	20.8	17.7	13.8	12.8	10.6	0.188	0.133	0.114	130	123	124
	GR-I	14.60	7.55	2.02	34.9	28.5	13.3	18.1	14.2	8.5	0.412	0.265	0.152	232	176	217

100° C. Butaprene-NM (butadiene-acrylonitrile copolymer), on the other hand, shows a very high value of $\omega\eta$ at room temperature, which rapidly decreases with increasing temperature while G remains high, so the heat generation at constant stress (H_σ) is not extremely large. All of these synthetics have considerably higher values of $\omega\eta$ than Hevea at the three temperatures employed, both in gum and tread formulas. It is apparent, however, that the addition of carbon black affects the synthetic rubbers to quite different degrees. For example, Butaprene-NM at 100° C shows the highest values of $\omega\eta$ and G of all synthetics in the gum formula, but gives the lowest values in the tread formula. The molecular hysteresis defect g, on the other hand, orders the rubbers in the same manner in tread stocks as in gum stocks at 50° and 100° C, except for the reversal between GR-S and Neoprene-GN at 100° C. The positive temperature coefficient found in g for the GR-S tread stock constitutes an example of a result which might be misleading in the development of synthetic polymers, if g alone were employed as the hysteresis index. In all cases, the static modulus G_{St} is lower than the dynamic modulus G. In many cases, G and G_{St} do not correlate. For example, GR-S and Neoprene-GN tread stocks appear softer than Hevea when measured statically (G_{St}), but have higher dynamic modulus values (G). Thus, static measurements of modulus or hardness often give misleading results when applied to solid or pneumatic tire design. It should be emphasized that neither H_ϵ) proportional to $\omega\eta$) nor H_σ completely describes the relative heat generation of tread stocks in service. Until more complete knowledge of their relative importance in tread service is obtained, tread compounding must remain a somewhat uncertain science. However, a reduction of $\omega\eta$ with no corresponding decrease in modulus G will always give a cooler running tread, providing the temperature coefficients of both quantities are properly considered.

ACKNOWLEDGMENT

The authors wish to thank various members of the Firestone technical organization for their cooperation in this work, particularly O. D. Cole, who compounded the various stocks employed, and R. F. Dunbrook and staff, who furnished the synthetic polymer samples. The continued interest of J. N. Street in the project is much appreciated, as is also the permission of The Firestone Tire & Rubber Company to publish these results.

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THE RETRACTION OF STRETCHED RUBBER *

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For some time we have been making measurements of the velocities acquired by rubber strips when retracting after being stretched. The rubber band is stretched in front of two photocells, cutting off two sharply focussed light beams. When the strip is released, the beams impinge successively on the photocells, the first of which starts the charging of a condenser, and the second of which stops the charging current. The resulting voltage on the condenser is thus a measure of the time required for the free end of the rubber strip to traverse the distance between the two light beams. Retraction velocities of the order of several hundred miles per hour have been observed.

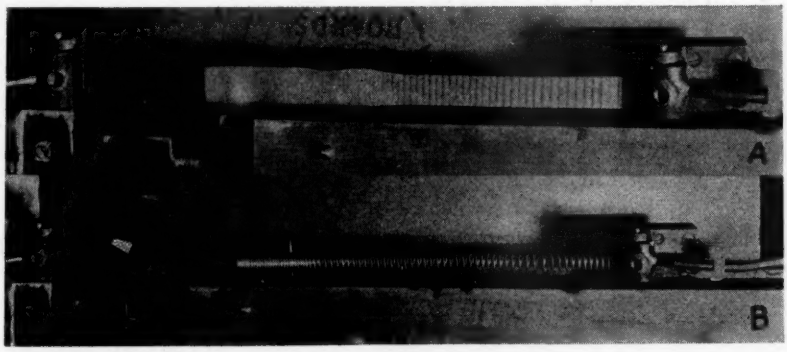

FIG. 1.

To explain some of our results and to secure a more detailed picture of the mechanism of retraction, we have also taken pictures of retracting rubber strips, with a high-speed stroboscopic lamp. These seemed to be of sufficient general interest to present here.

Parallel equidistant lines were ruled across the strips before they were stretched. The spacings of these lines were then measured in the photographs of the retracting strips to study the local elongation at any point during the retraction.

The photographs show that a rubber stock having low internal friction, such as a Hevea-rubber cured gum stock, retracts very much like a steel spring. The retraction starts at the released end, and progresses in a wave until it reaches the stationary end. This effect is shown in the photographs of Figure 1 and also by the measurements of local elongation, taken from the photographs, which are plotted in Figure 2.

* Reprinted from *The Physical Review*, Vol. 65, Second Series, Nos. 7 and 8, page 250, April 1 and 15, 1944.

It is interesting to note that the sharpness of this retraction wave front depends on the internal friction of the elastic material. Butyl-rubber gum stocks show practically no wave front, but merely a progressively lower elongation along the strip.

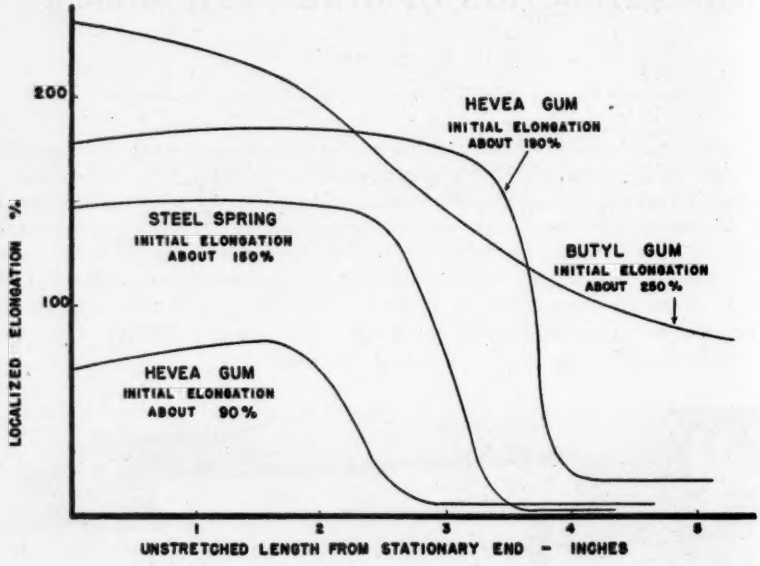

FIG. 2.—Local elongation *vs.* unstretched length.

It is planned to publish a complete description and the results of the experiments at an early date.

EFFECT OF TEMPERATURE ON THE MECHANICAL PROPERTIES OF RUBBERLIKE MATERIALS *

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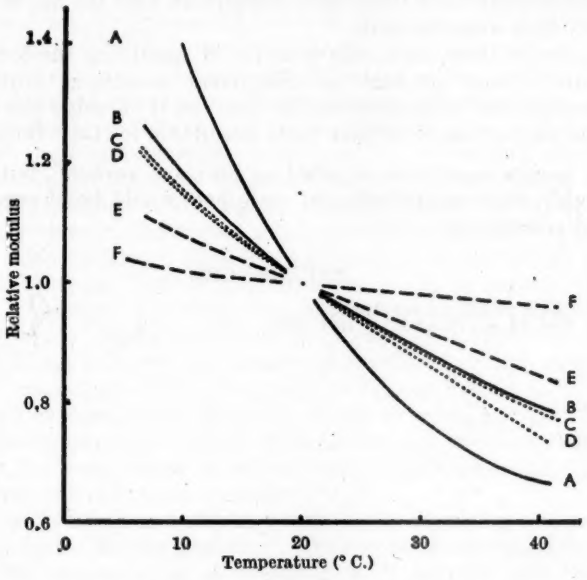
In the course of investigations into the mechanical properties of natural and synthetic rubbers intended for use in antivibration devices, variations of a large order were encountered. As these variations seemed to be largely dependent on temperature, a preliminary detailed examination in the region of 5° to 40° C was made. With the aid of a mechanical vibrator somewhat similar



to that employed by Gehman[1], and working at 20–60 c.p.s., measurements of dynamic elastic compression modulus and associated resilience were made by the well known resonance method. A detailed description of the apparatus, method, and results is to be published later; for the present time, it may be said that the test-pieces were in the form of cylindrical rubber blocks, 0.875 inch in diameter and 0.875 inch high, bonded at each end to steel screws by the conventional brass-plate method.

In determining the use of an elastic material as a vibration insulator, the dynamic modulus (in compression and (or) in shear) is of paramount importance. In comparing the variations in temperature of a wide range of materials from very soft to very hard ones, a plot may be made of relative modulus

* Reprinted from *Nature*, Vol. 153, No. 3881, pages 341–342, March 18, 1944.

as a function of temperature, i.e., the modulus at the stated temperature divided by the modulus at some standard temperature, which in the present case was 20° C.

Some early results are illustrated by the curves in the diagram. The area enclosed by the solid lines A and B shows the variation of the modulus-temperature effect in a comprehensive series of Neoprene-E mixtures, the dotted lines C and D show the effect for a range of GR-S mixtures, and finally the broken lines E and F show the effect for a series of natural-rubber mixtures analogous to those in GR-S.

The purpose of this note is to direct attention to the following facts in connection with rubberlike materials intended for use in antivibration devices.

1. The dynamic modulus has a considerable temperature coefficient.
2. Quite apart from temperature variations likely to be encountered in service, this fact is of importance in the quoting of dynamic results. The temperature of testing should always be stated.
3. No sign of a temperature effect of this order is evident from static loading tests; in the present work these were carried out with the aid of a well-known torsion flexibility measurement.
4. In view of these facts, the practice of specifying the low-remperature requirements of such products as instrument mountings (antivibration) in terms of a static test is likely to lead to wastage of valuable raw materials and labor in the production of articles quite unsuitable for their intended purpose.

Similar results have been reported by previous workers[2], but it is felt that a considerably wider appreciation of such facts would be of general benefit in the present emergency.

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RHEOLOGICAL PROPERTIES OF NATURAL AND SYNTHETIC RUBBERS *

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THE FIRESTONE TIRE & RUBBER COMPANY, AKRON, OHIO

One of the important factors determining the processing characteristics of a rubber or unvulcanized rubber stock is the "plasticity". This term has been used by rubber technologists to define the rate at which a material can be made to flow under a set of conditions of stress, geometry, and temperature. Strictly speaking, plasticity is not a quantitative term but, because of past usage, it seems justifiable to continue to employ it as an inverse index of resistance to flow. Three principal types of instruments have been employed for measuring plasticity of rubberlike materials: parallel plate, rotating disk or cylinder, and extrusion plastometers. The parallel-plate type[1], like the rotary type plastometer[2], is designed to operate with no slippage between rubber and confining surfaces, and both operate at rather low rates of shear. The rotating disk plastometer[3], however, permits attainment of thixotropic equilibrium and simple calculation of the mean shearing stress at a given average rate of shear. All extrusion plastometers described in the literature[4] have employed rather short, large bore extrusion tubes, which permit appreciable slippage between rubber and tube walls, and have operated at a constant driving pressure and temperature, the rate of efflux serving as the plasticity index. The existence of slippage, of course, eliminates the possibility of calculating absolute consistency (inverse of plasticity), but is an advantage in that factory processing conditions[5], where slippage is a factor, are simulated. High rates of shear of the order of magnitude of those existing in factory extruders may be readily attained with extrusion plastometers. It has been argued[6] that high rates of shear in a plastometer are desirable from the standpoint of predicting processability, since the shear stress *vs.* rate of shear relationship for rubberlike materials departs radically from linearity.

For natural rubber and stocks based on it, plasticity appears to be the predominant factor in processability[7]. Hence, without regard to the relative virtues of the various types of plastometer, it may be said that plasticity measurements, if properly interpreted, are quite sufficient for the prediction of the behavior of natural rubber in factory processing operations. For synthetic rubbers of the butadiene-styrene or butadieneacrylonitrile copolymer types, however, the measurement of plasticity alone does not suffice. Apparently, hot tear resistance of the crude synthetics, which is much lower than that of natural rubber, is also an important factor, and it is possible that other properties, not yet clearly defined, are involved. In spite of these complicating factors, it nevertheless appeared desirable to devise an improved extrusion plastometer in which the characteristic high rates of shear could be attained but with which more reliable shear stress *vs.* rate-of-shear curves could be obtained. This has been accomplished by the use of a long, small-bore tube

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and a constant rate of piston travel, the shear stress at a given rate of shear being measured.

The advantage of measurement at a constant average rate of shear is evident from the form of the shear stress *vs.* rate of shear curves of Figure 3. Since the rate of shear increases rapidly with increasing shear stress at high rates of shear, small differences between the rheologic properties of different samples, or unavoidable minor changes in the driving pressure of a constant-pressure type of plastometer, may lead to large and sometimes spurious differences between their rate-of-shear plasticity indices. Thus, for maximum precision, the constant-speed type of measurement appears desirable, particularly for synthetics, which yield somewhat flatter stress *vs.* rate-of-shear curves.

APPARATUS AND TECHNIQUE

The instrument used in these experiments is shown in Figure 1. The sample is preheated in chamber *A* and extruded through the die, shown at *H*. The chamber is formed of two parts, the upper portion of which *B* is fixed in

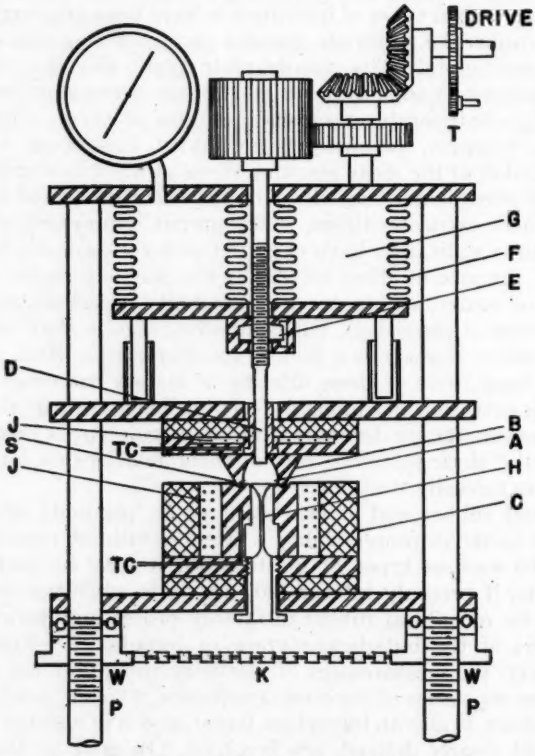

FIG. 1.—Diagram of the constant-speed plastometer.

position with respect to the frame of the instrument. The lower portion *C*, which contains the capillary, can be raised and lowered by means of sprocket wheels *W* which are threaded internally to permit motion up and down along the support posts *P*. These wheels are joined together by a roller chain *K*

so that they move together. The rubber sample, of thickness greater than the height of the chamber, is laid on the top surface of the lower member C while the latter is in its lowered position. When the lower part of the chamber is raised into contact with the upper part at seal S, the rubber is forced into chamber A, the excess being extruded through the capillary and seal. The sample is preheated 10 minutes at temperatures of 120° C or below before the extrusion piston D is started downward.

The Bakelite spline gear at the top is driven at a constant rate by a motor and gear train. Turning this gear drives the plunger D into the chamber by thrusting the threaded portion of the plunger shaft against nut E. The total stroke of the plunger is 32 mm. The resistance of the specimen to the progress

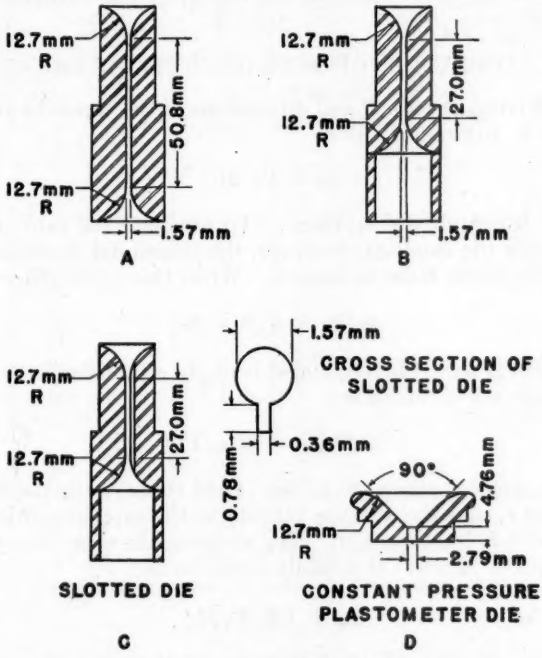

FIG. 2.—Details of extrusion capillaries.

of the plunger is communicated through this nut to floating plate F and thence to oil-filled metal bellows G, whence it is registered as hydrostatic pressure by a large Bourdon gauge, which was calibrated against a dead load on the plunger. As the plunger displaces the specimen in the chamber, the specimen is extruded at the chosen rate through capillary H. A variable-speed motor, coupled to the driving gear train through a pair of cone pulleys, permits the rate of piston travel and, consequently, the average rate of shear, to be varied in small steps over a large range. The average rate of shear is indicated by a tachometer attached to the gear train at T. The capillaries are easily interchangeable, so that different forms can be used without other change in the instrument. The chamber and capillary are held at the selected temperature by means of the heater windings shown at J, and are insulated from the frame of the instrument by plates of Transite, as shown. The temperature of the two parts of the

chamber is measured and controlled by means of thermocouples *TC*, which actuate a potentiometer controller-recorder.

By means of this arrangement it has been found possible to determine equilibrium values of shear stress at average rates of shear from 5 to 100 $sec.^{-1}$. Since the portion of the specimen in the chamber is not altered appreciably (most of the shearing taking place in the capillary), it was found practical to test at as many as four rates of shear with one filling of the chamber. The apparatus required about ten grams of material for each filling of the chamber. In the initial tests, two capillaries were used; the first was 2 inches long, and 0.062 inch in diameter. The second was 1.062 inches long and 0.062 inch in diameter. The capillaries are of the form shown in Figure 2. The lengths given are those of the narrow part of the die, and do not include the trumpet-shaped entrance.

CALCULATION OF AVERAGE RATE OF SHEAR

When the driving presure P and dimensions of the capillary are known, the shearing stress at any radius r is:

$$S_r = Pr/2L \tag{1}$$

where L is the length of the capillary. To calculate the rate of shear at the same point within the capillary, however, the functional dependence of rate of shear on shearing stress must be known. When this dependence is linear, *viz.*:

$$dv/dr = K(S - S_0) \tag{2}$$

the velocity front is paraboloidal, and it is easily established[6] that the volume-weighted average rate of shear is:

$$(dv/dr)_{Av} = 32v_{Av}/15R \tag{3}$$

where S is the shearing stress, S_0 is the "yield stress", v is the linear velocity of flow at radius r, v_{Av} is the average velocity in the capillary, R is the radius of the capillary, and K is a constant. The shearing stress on the cylindrical surface defined by $v = v_{Av}$ and (3) is easily found to be:

$$S_{Av} = PR/2\sqrt{2}L. \tag{4}$$

Now the rate of shear *vs.* shearing stress relationship for rubberlike materials is far from linear (see Figures 3–9) and hence, strictly speaking, Equations (3) and (4) do not apply. Nevertheless, for the higher rates of flow, the departure from linearity is not great, and there is some justification for plotting the shearing stress defined by (4) against the average rate of shear given by (3), rather than pressure against rate of efflux. This procedure has been followed throughout this work with the object of obtaining rheological curves which become approximately independent of the capillary dimensions when the linear law of flow (2) is approached at the higher rates of flow and wall slippage is negligible. It is acknowledged that, when curves obtained with a given sample with different capillaries do not coincide, this method of representation yields no information which could not be obtained by plotting pressure against efflux rate. Where the curves for different capillaries coincide, however, this method is convenient since it permits an inference that wall slippage and resistance to flow in the entrance of the capillary are small.

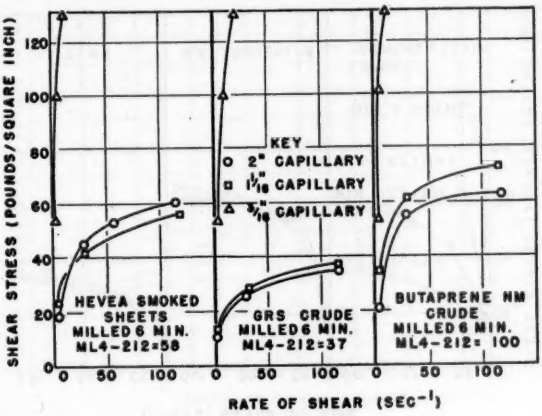
SHEAR STRESS (POUNDS/SQUARE INCH)
RATE OF SHEAR (SEC⁻¹)
KEY
2" CAPILLARY
1/16 CAPILLARY
3/16 CAPILLARY
HEVEA SMOKED SHEETS MILLED 6 MIN. ML4-212=58
GRS CRUDE MILLED 6 MIN. ML4-212=37
BUTAPRENE NM CRUDE MILLED 6 MIN. ML4-212= 100

FIG. 3.—Effect of capillary geometry.

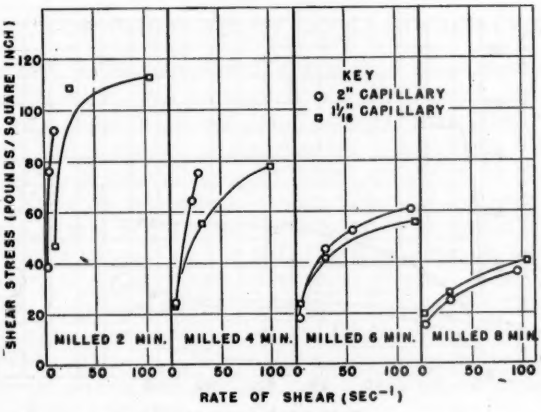

FIG. 4.—Effect of capillary geometry—Hevea smoked sheet.

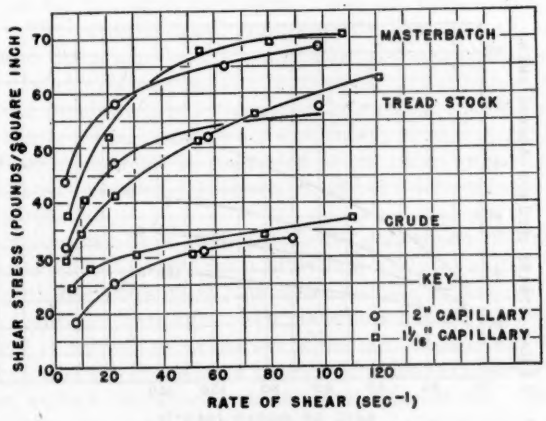

FIG. 5.—Effect of compounding—GR-S.

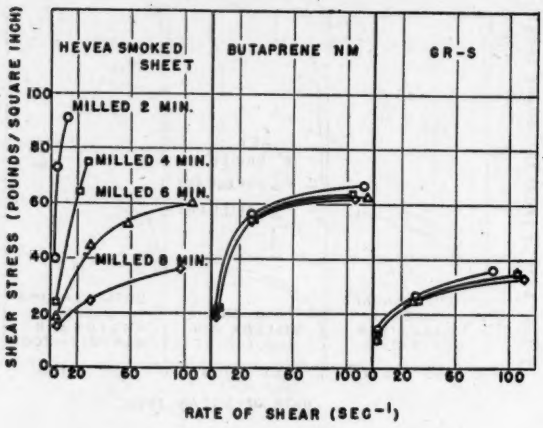

FIG. 6.—Effect of milling.

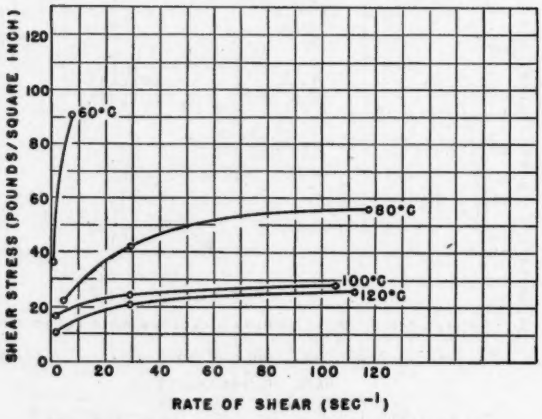

FIG. 7.—Effect of temperature—Hevea smoked sheet.

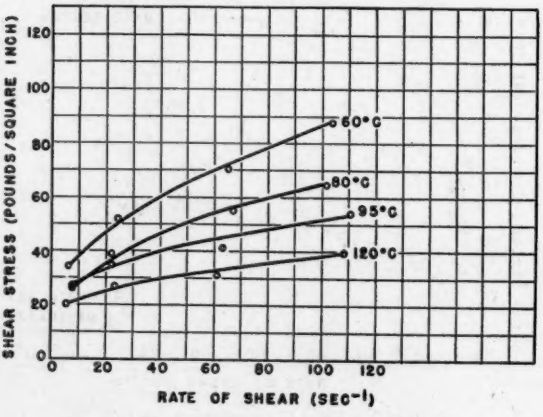

FIG. 8.—Effect of temperature—Butaprene-NM.

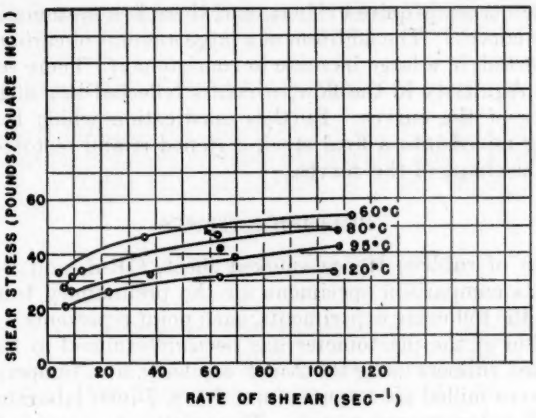

FIG. 9.—Effect of temperature—GR-S.

EFFECTS OF VARIATION OF CAPILLARY DIMENSIONS

Portions of each sample employed in this experiment were masticated on a 2.5 × 7-inch laboratory mill for periods of 2, 4, 6, and 8 minutes. The resulting specimens were each divided into two parts for testing. Capillaries *A* and *B* (Figure 2) were used, and the chamber temperature was 80° C in all cases. The results on uncompounded rubbers are shown in Figures 3 and 4. The calculated shear stresses generally were lower for the long capillary than for the short one, except in the cases for unmilled or undermilled Hevea rubber (Figure 3). After 8 minutes on the mill, the Hevea sample had become very tacky and the longer capillary gave lower shear stresses, as in the cases of the synthetic rubber specimens. The curves for the two capillaries agree best where the flow most closely approaches the Bingham type given by Equation (2), in agreement with theory. Where this approximate coincidence is obtained, at least, it appears safe to assume that wall slippage and resistance to flow in the trumpet entrance are small.

On the same scale of Figures 3 and 4 are shown the constant pressure plastometer data for the same specimens. The die used in this case is shown in Figure 2D. The rates of shear, computed by Equation (3), are seen to be far smaller than is demanded by the magnitudes of the applied shearing stresses. Since relatively large wall slippage in the short die would yield just the opposite result, it must be concluded that friction in the entrant cone is the predominant factor in this effect. This result is not surprising, since a much larger fraction of the applied pressure must be expended in shearing the portion of the material in the entrant cone of the short, large-bore die compared to the long, smaller bore tubes.

Mooney plastometer data (ML-4-212) are also given in Figure 3. They represent torques with the large rotor after four minutes at 100° C. The high torque found with the Butaprene-NM seems to be a consequence of operation at a low rate of shear. Here again, the measured quantity is the ordinate of a steep curve, and is subject to variations which are misleading.

Figure 5 indicates the correlation between the two capillaries for samples of GR-S polymer, carbon black masterbatch, and tread stock. These tests were made at a chamber temperature of 100° C. Here the shifting of the relative

positions of the curves is quite evident, and there is a systematic difference in the form of the curves. The addition of a large amount of carbon black results, as is to be expected, in a large increase in consistency. There seems also to be somewhat less regularity in the flow, which is reflected in a slight decrease in the smoothness of the curves. Further mastication which the material received in being mixed into a final stock softened it and restored much of the regularity to the shape of the curves.

PRECISION TESTS

Three types of rubber, Hevea smoked sheet, GR-S, and Butaprene-NM, were selected as comparison specimens for the preliminary testing of the instrument. In the following experiments, each point represents a single reading.

The precision of the plastometer has been determined in the cases of the three comparison rubbers using the 2-inch capillary, at a temperature of 80° C. The samples were milled six minutes on a 2.5 × 7-inch laboratory mill. Ten samples of each polymer were tested. The results are given in Table I.

TABLE I

REPRODUCIBILITY OF CONSTANT SPEED PLASTOMETER DATA. AVERAGES OF 10 MEASUREMENTS

Material	Treatment	Tube length (mm.)	Temp. (° C)	Rate of shear ($sec.^{-1}$)	Average shear stress (lbs. per sq. in.)	Average deviation (lbs. per sq. in.)	Average deviation (±%)	Range (±%)
GR-S	Milled 6 min.	50.8	80	5	16.3	0.5	3.1	6.7
				30	28.4	0.2	0.7	1.4
				100	36.6	0.9	2.5	4.5
Butaprene-NM	Milled 6 min.	50.8	80	5	22.7	1.7	7.5	13.2
				30	49.6	1.1	2.2	3.5
				100	61.4	0.9	1.5	3.2
Smoked sheet	Milled 6 min.	50.8	80	5	22.4	0.7	3.1	10.4
				30	40.4	1.6	4.0	8.4
				100	64.3	2.7	4.2	7.0
GR-S	Unmilled	27	100	5	22.1	1.3	5.9	13.1
				30	32.9	0.6	1.8	4.2
				100	36.4	1.6	4.4	6.5
GR-S tread stock		27	100	5	30.1	2.1	7.0	13.0
				30	51.2	0.4	0.8	2.2
				100	54.7	0.7	1.3	2.8

For purposes of comparison, values of shear stress at 5, 30, and 100 $sec.^{-1}$ were read from the curves, and from these the average deviation and fractional ranges were determined. It should be noted that these indices depend to a considerable extent on the material being tested, and that the precision is greater at the higher rates of shear. The curves are, in the main, self-consistent; that is, the curves for individual tests tend to be above or below the average for their entire length and, in a majority of cases, do not cross. An estimate of the instrument's precision was also made for an unmilled GR-S rubber and the tread stock made from it (at 100° C, using the 27-mm. tube). These results are also shown in Table I. In this case the ten samples were tested alternately, tread and polymer, to decide whether the material held over in

the capillary after any test would affect the succeeding test. No such effect was observed.

COMPARISON OF RESULTS OF VARIOUS PLASTOMETERS

The correlation between the results of the constant-speed plastometer and those of the Firestone constant pressure plastometer and the Mooney plastometer is indicated in Table II. Six batches of crude GR-S, representing six

TABLE II

COMPARISON OF PLASTOMETERS

Sample	Constant-speed shear stress, at indicated rate of shear (lbs. per sq. in.) 100° C				Constant pressure plastometer (seconds at 1960 lbs. per sq. in.)	Mooney plastometer	
	5 sec.$^{-1}$	25 sec.$^{-1}$	60 sec.$^{-1}$	100 sec.$^{-1}$	80° C	ML4-212 100° C	MS4-212 100° C
Crude GR-S							
1	24.0	30.4	32.7	34.0	8.8	61	—
2	21.0	30.0	33.0	35.4	14.2	63	—
3	21.7	29.0	33.7	39.0	10.0	66	—
4	21.4	30.7	34.7	37.7	15.0	69	—
5	20.7	29.7	36.0	41.0	8.5	73	—
6	29.7	36.7	41.0	44.7	12.0	78	—
GR-S Masterbatch							
1	45.4	66.0	71.7	74.4	14.4	—	79
2	36.6	56.0	67.0	70.0	11.0	—	75
3	43.3	61.4	68.4	70.4	13.4	—	75
4	38.4	58.5	68.5	72.7	12.0	—	76
5	36.7	58.0	68.8	74.1	13.6	—	81
6	41.6	63.3	71.8	74.6	12.6	—	82
GR-S Tread stock							
1	29.6	42.3	53.4	60.0	—	—	53
2	26.6	42.0	53.0	56.0	10.8	—	47
3	31.9	42.3	52.0	56.6	9.8	—	53
4	36.6	52.3	58.3	60.0	9.6	—	54
5	35.0	49.6	58.3	63.0	9.8	—	56
6	38.6	56.0	62.2	66.0	9.2	—	62

factory polymerizations, were employed. The constant-speed plastometer data are interpolated to rates of shear of 5, 25, 60, and 100 sec.$^{-1}$. The constant pressure plastometer results are expressed as time (seconds) to extrude 5.70 cc. of rubber at 80° C with a driving pressure of 1960 lbs. per sq. inch. The Mooney plastometer data (ML 4–212) are torques after 4 minutes of rotation, using the large rotor for the crude materials. In the case of the black masterbatches and final stocks, the small rotor was used and the torque expressed as (MS 4–212).

The correlation between constant-pressure and constant-speed extrusion instruments is not very good, except in a general way. The constant-pressure instrument was rendered too sensitive to small variations by the flat form of the curve for crude GR-S. Agreement between the two was better in the case of the masterbatch, probably because of the steeper stress-rate of shear relationship. Fairly good agreement was observed between the Mooney and the constant-speed instrument, the best correlation being found when the constant speed machine was operated at a high rate of shear. This unexpected type of correlation cannot be considered general since, for some other materials, the constant-speed data at the lower rates of shear have been found to agree better

with the Mooney results. General correlation for all rates of shear could not be expected, of course, since the curves cross each other in many cases.

EXPERIMENTS WITH SLOTTED DIE

To obtain directly some idea of the relation between indications of the plastometer and processing quality, a die of the form shown in Figure 2C was used. This die has been slotted, so as to introduce radical gradients in the shear stress. The plastometer was operated at a high rate of shear and the gauge pressure recorded. These data were not reduced to absolute values, since the shape of the cross-section of the die would make such calculations uncertain. An N-type of Butaprene masterbatch was subjected to oven heating for periods up to 90 minutes, and the gauge pressure for a fixed high

TABLE III

RELATION BETWEEN APPEARANCE AND CONSTANT-SPEED PLASTOMETER DATA

Sample	Time at 150° C (min.)	Appearance		Gauge pressure (lbs. per sq. in.)
		Body	Thin section	
1	0	Smooth	Smooth	6.5
2	15	Slightly rough	Sheared off	7.5
3	30	Rough	Small, torn	8.1
4	45	Rough	Small, torn	9.1
5	60	Rough	Scraps only	9.8
6	90	Rough	Scraps only	10.7

rate of shear was recorded. The extruded pieces were inspected with regard to the condition of the thin section, and the overall roughness of the cylindrical section. Appearance ratings were made and correlated with plastometer gauge pressures. Some typical data are given in Table III. It is apparent that, for this one parameter, the instrument indicates differences in tubing quality.

EFFECTS OF MILLING AND TEMPERATURE

The effect of milling on the three types of material is demonstrated by the curves of Figure 6. The samples were masticated on the 2.5 × 7-inch laboratory mill for periods up to 8 minutes. The action of this small mill is very severe. Hevea smoked sheet, very stiff before milling, broke down rapidly, and became excessively tacky after 8 minutes on the mill. It will be noted that this highly masticated material gave a curve which most nearly resembled that of GR-S. A very small amount of softening was observed in GR-S and in Butaprene-NM after 8 minutes on the mill. In these materials there were no evident surface changes, as was the case with Hevea. These curves appear to define the problem of processing evaluation of the synthetic rubbers, in this respect: that no one point on the rheologic curve is sufficient to describe the behavior of the material in shear. If the parameters are suitably chosen, the materials can be made to appear very similar, or quite different.

The effect of temperature on plasticity differs considerably from one type of polymer to another. In all the cases examined, the materials were found to be softer at higher temperatures, and no significant anomalies were observed. Milled Hevea smoked sheet (see Figure 7) was found to soften very rapidly with increasing temperature, and seemed to approach a limiting value of plasticity somewhat above 120° C. At the elevated temperature the rubber became rather tacky. Butaprene-NM and GR-S exhibited similar effects, but

on a much smaller scale (Figures 8 and 9). The synthetic polymers showed little or no tendency to approach a limiting value of plasticity with increasing temperature. The tests at 95° C and 100° C may be observed to give plots which are much flatter than those at higher or lower temperatures.

DISCUSSION

In general, it may be said that the unmilled butadiene-styrene and butadiene acrylonitrile rubbers studied resist flow with a shear stress which increases less rapidly with increasing rate of shear than is the case with unmilled or slightly milled Hevea rubber. They resemble milled Hevea rubber in their stress *vs.* rate-of-shear characteristics, both in type and in magnitude. However, the rates of breakdown on the mill are much lower for these synthetics, and they exhibit much smaller temperature coefficients of plasticity than those of Hevea rubber. In these respects, then, some of the processing difficulties encountered with these synthetics are explained by rheological experiments. To define processability completely, however, plasticity must be considered only one important factor, and means of measuring other variables such as tear resistance and "shortness" must also be devised.

No attempts have been made in this paper to analyze the data in terms of current theories of molecular structure. Suffice it to say that the rate of shear *vs.* shearing-stress data does not yield straight lines when plotted in semilog graphs. Thus, the simplest form of the activation rate theory of Tobolsky and Eyring[8] does not appear to hold for these experiments. The application of more exact forms of the theory, however, might give better agreement. The data do give straight lines in log-log plots but this fact, often observed with data of this type, appears to have little theoretical significance.

ACKNOWLEDGMENT

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GR-S, AN ELASTICALLY INVERTED POLYMER *

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INTRODUCTION

To the compounder faced with the necessity of making tires of GR-S, three main problems need to be faced; (1) processing and handling, including building tack; (2) hot running of the tires on test wheel or road, and (3) heat embrittlement and flex-crack growth.

Ways and means have been devised to make processing of GR-S possible, even though not so easy as with natural rubber.

Laboratory investigation of the hysteresis and heat build-up characteristics of GR-S has so far followed closely the lines developed for natural rubber. These fall into distinct types. Probably the oldest are rebound tests. Rubber balls are dropped onto solid steel plates or, conversely, steel balls are dropped onto firmly supported rubber test slabs. The Lüpke pendulum[1] employs a horizontal ram with a double V filar suspension. The pendulum with a rigid arm by which the degree of penetration of the hammer may also be determined[2] has found wide acceptance as a means of measuring impact resilience.

The damping effect on free vibration of rubber members is measured on an oscillograph[3] or a torsion pendulum[4] as a means of evaluating hysteresis.

Much ingenuity has been shown in the various forms of flexometers which have been developed to duplicate to a greater or lesser degree the amplitude and frequency of vibration and load carrying conditions of service[5] to predict heat build-up.

These tests have two things in common. They subject the specimen to relatively low deformations, and they show GR-S to have greater hysteresis than natural rubber. Useful as flexometer tests are in predicting heat build-up of rubber when used as a shock absorber, they throw no light on the mechanism of failure of GR-S due to rapid flex cut growth. This is particularly true when these tests are carried out in the laboratory under substantially isothermal conditions and at ordinary room temperatures[6]. The obvious reason is that the deformations induced fall far short of the strains just antecedent to rupture.

The problem, therefore, demanded the study of rubber stretched nearly to rupture.

STRESS RELAXATIONS (WITH TIME)

One of the first manifestations of abnormal stress relaxation of GR-S is Shore creep, announced by Columbian Carbon Company Laboratories[7] and confirmed by the Bureau of Standards[8]. This phenomenon has necessitated a new specification for hardness determinations, *viz.*, the reading of hardness values at 30 seconds after application of the Durometer or penetrometer. This relaxation or creep is so characteristic of GR-S that it was successfully employed as a rapid means of distinguishing GR-S treads from those of natural rubber in a series of captured tires submitted for physical testings.

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Shore creep is primarily a relaxation of strain, but does involve an accompanying decrease in applied stress. In extending the study of stress relaxation with time to greater deformations than those involved in hardness testing, elongations were maintained constant. Table I summarizes the relaxations in

TABLE I

STRESS RELAXATION OF NATURAL RUBBER AND GR-S TREAD STOCKS

Elongation (percentage)	Relaxation in stress (lbs. per sq. in.)		Time (min.) of relaxation	Condition of test
	Natural rubber tread	GR-S tread		
100	100	135	30	80° F
400	735	670	30	80° F
400±10	670	600	30	80° F with jiggle*
100	135	150	30	130° F
200	200	235	30	130° F
300	400	335	30	130° F
400	600	535	5†	130° F

* A mean elongation of 400 per cent was maintained; but the specimen was jiggled between 390 per cent and 410 per cent elongation at a frequency of 350 cycles per minute.
† GR-S sample broke in 5 minutes.

stress (in lbs. per sq. in.) of natural rubber and GR-S treads when stretched to various elongations.

There is a definite indication that both at room temperature (80° F) and at even a slightly elevated temperature there is a reversal in the relative amounts of relaxation, *i.e.*, at low elongations GR-S relaxes more, but at the higher elongations it relaxes less. These data, particularly at 400 per cent elongation, suggest a relative tightening or shortening of GR-S at higher elongations, particularly when hot. The effects shown were not of the order of difference between GR-S and natural rubber when tested for flex-crack growth and heat embrittlement where GR-S rates only from about 2 to 30 per cent of natural rubber.

In the case of a flex-cut growing in a running tire tread, the conditions are widely different from those of the above test. The element of rubber at the apex of the tear is stretched and relaxed during about $\frac{1}{6}$ of the revolution of the wheel, and is then allowed to recover for the other $\frac{5}{6}$ of the revolution. In a tire as a whole, the degree of deformation is limited by the relative inextensibility of the carcass cords, and within these limits is controlled by load and inflation pressure. It is of low amplitude, corresponding probably to not more than about 50 per cent elongation. However, for the element of rubber being abraded or chunked out, and for the element undergoing tear at the apex of a flex-cut, the deformation must reach that of rupture.

This, therefore, called for a study of the stress-strain properties of flexed rubber where the maximum amplitude of extension is increased to near rupture.

HYSTERESIS AT HIGHER ELONGATIONS

Resource was had to the much disparaged hysteresis loop determined on a tensile testing machine, with jaws moving 18 inches per minute. This is far from the rate of movement in a tire, but it does remove the stress completely as in a rolling tire, and its slow speed may be assumed to compensate somewhat

for the fact that, as pointed out, the rubber in the tire is free to recover under its own retractive forces for 5/6 of the time of the complete cycle.

A typical set of hysteresis loops for natural and GR-S treads is shown in Figure 1. The maximum elongation of the loop is increased up to 400 per cent.

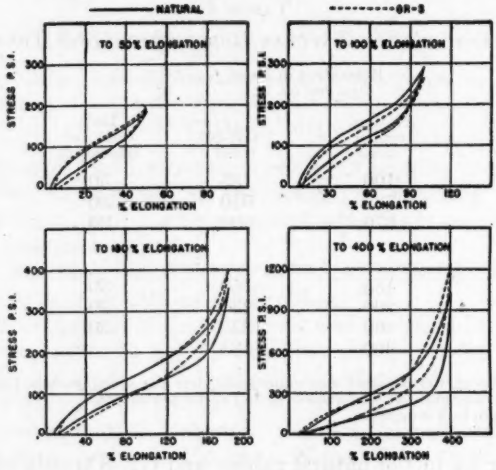

FIG. 1.—Hysteresis loops. · Natural rubber and GR-S treads (10th loop).

Approximate equilibrium was reached in 10 cycles. At 50 per cent elongation, GR-S shows 35 per cent more hysteresis than does natural rubber. At about 100 per cent elongation it has the same hysteresis and, at 400 per cent elongation, GR-S actually has only about 80 per cent of the hysteresis of natural rubber (Figure 2).

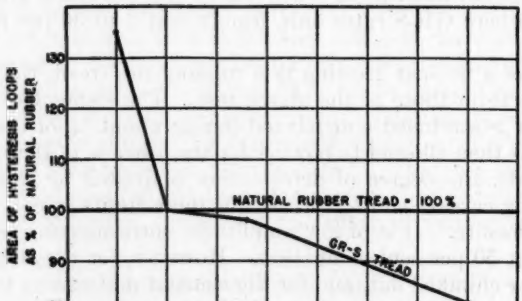

FIG. 2.—Effect of elongation on hysteresis of GR-S and natural rubber.

This fact in itself is not new, having been disclosed by Rohde[9] in 1939. In this case the determinations were made to fixed stress, and it was shown that rubber relaxed much more, *i.e.*, stretched much farther under repeated cycles, and also showed more hysteresis at the higher stresses than did Buna-S (Figure 3—from Rohde).

There thus appears to be a contradiction between laboratory testing and road service, as pointed out by Sebrell and Dinsmore[10] in 1941, who commented on Rohde's work as follows:

"Hysteresis loops, secured in the normal manner with a tensile testing machine, indicated that after ten cycles the energy loss for a natural-rubber tread stock was about six times as great as for a Buna-S tread. In actual tests

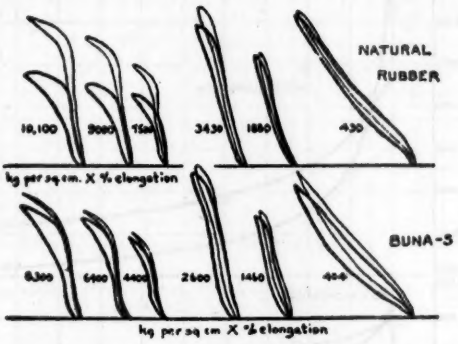

FIG. 3.—Comparison of the hysteresis of Buna-S and natural rubber with increase in energy absorbed (see Reference 9).

on tires, the Buna-S tread, however, did not run at a lower temperature when compared with the natural rubber tread.

"Hysteresis loops were then obtained for various ranges of elongation. It was found that, for the tread stocks tested, natural rubber was superior in elasticity and work capacity for tensile stresses below 35 kg. per sq. cm. Only above this stress was Buna-S superior. Consequently, this advantage did not show up when the stocks were employed as tire treads.

"In the same vein, many of the apparently contradictory test results for synthetic rubbers will probably, at some future time, find a logical explanation".

STRESS RELAXATION WITH FLEXING

It is believed that the present approach, *viz.*, a study of the effect of increasing strain on the stresses developed in flexed rubber, will resolve this apparent contradiction. If, instead of showing the increase in strain with repeated flexing, as Rohde did, the resultant stresses to the various elongations are plotted against the number of flexings (Figure 4), it is seen that, for elongations below 100 to 150 per cent elongation, both rubbers relax to about the same degree. At 180 per cent elongation, although the natural rubber had the higher initial stress or modulus, even at the second cycle, it had softened more than the GR-S. At 400 per cent elongation, however, this difference is much greater, so that at equilibrium the GR-S tread, instead of being 500 pounds lower in modulus, is now 200 pounds higher in modulus than is the natural rubber tread. This is summarized in Figure 5. Translating this into performance in a tire, it is seen that, if an element of tread rubber is strained repeatedly to about 400 per cent elongation, the GR-S develops a higher opposing stress than does the natural rubber tire. A flex-cut in this region is, therefore, pulled open with greater force.

Further, to illustrate this phenomenon, a series of dumbbell test-samples, cut from test sheets of tread-type compounds, were stretched to 400 per cent elongation and allowed to return to zero stress 10 times at a jaw separation and return rate of 18 inches per minute. They were then promptly put into

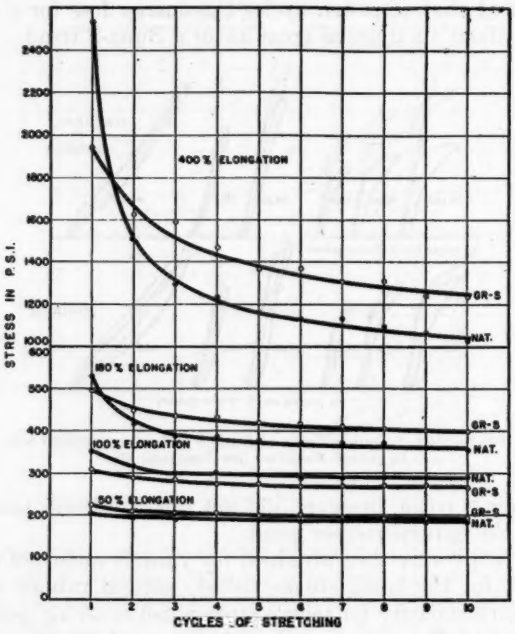

Fig. 4.—Stress relaxation with flexing to various percentage elongations.

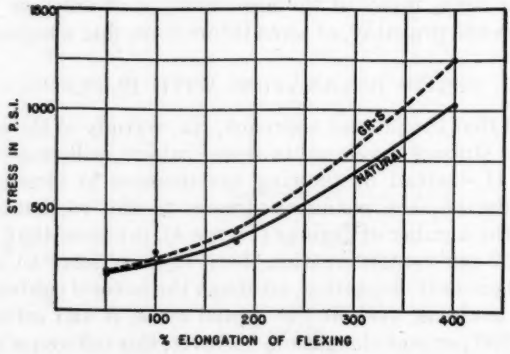

Fig. 5.—Effect of elongation on stress after flexing.

a Scott tensile tester, and stress strain curves were generated, using the original bench marks. The stress-strain curves for the unflexed rubbers were also generated.

Figure 6 shows the stress-strain curves of the natural rubber tread before and after the 10 flexings to 400 per cent elongation described above. It will be

noted that, until severe over-cures are reached, the effect is the equivalent of an extra elongation of about 100 per cent for all but the lowest stresses. This is generally described as due to subpermanent set, and it might be argued that new bench marks should be made after the flexing. However, the curves as they stand give a truer picture of the performance of the various tread elements.

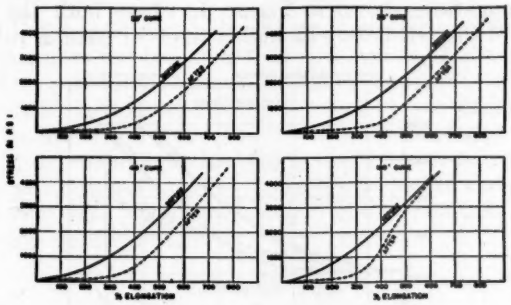

FIG. 6.—Stress strain curves—natural rubber tread before and after 10 flexings to 400 per cent elongation.

It is seen that after flexing to 400 per cent elongation the natural rubber becomes softer, its breaking elongation has increased by 100 per cent, and its breaking tensile has increased measurably. At severe overcures this softening due to flexing is not so great for the higher elongations. [The best cure for this compound was 30 min. at 280° F.]

Figure 7 shows a similar series of curves for the GR-S tread. Only at the lower elongations do the flexings to 400 per cent have a softening effect, but at

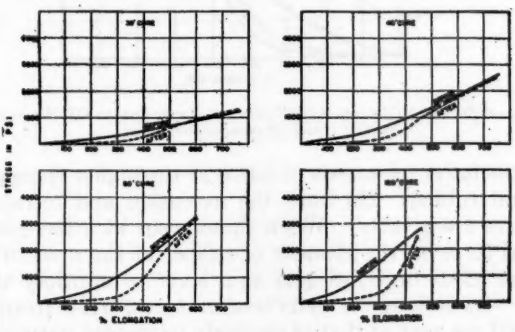

FIG. 7.—Stress strain curves—GR-S treads before and after 10 flexings to 400 per cent elongation.

500 per cent elongation and beyond, the "flexed" stress-strain curves coincide with the originals. This is true for all cures starting with a bad undercure. [The best cure for the compound was 45 min. at 280° F.]

In Figure 8 the data of Figures 6 and 7 are regraphed to facilitate comparison of the two rubbers at comparable states of cure, both before and after flexing.

At the 35 per cent undercure, the flexed GR-S builds up no more stress with elongation than does natural rubber. This is in agreement with road experi-

ence, which has shown better cut-growth performance for undercured tires. Unfortunately, their heat build-up at low elongations is excessive.

At best cures the stress-strain curves before flexing indicate that the GR-S tread is softer, but after flexing the relative positions are reversed, and GR-S, under forced vibrations beyond 300 per cent, builds up more resistance than does natural rubber. This confirms the inference from the hysteresis loops to 400 per cent elongation, shown in Figure 1, where both the extension and retraction arms of the GR-S loop lie higher than for natural rubber.

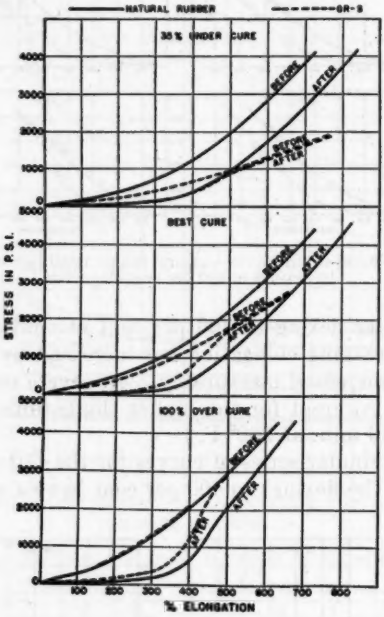

FIG. 8.—Effect of 10 flexings to 400 per cent elongation on GR-S and natural rubber treads at comparable cures.

Because of the lower hysteresis of GR-S at the higher elongations, it relaxes less than natural rubber. On both the extension and retraction cycles the developed stresses are greater. When these occur at a flex-cut, they increase greatly the total force on the element of rubber at the apex of the cut. This relaxation-failure effect of GR-S acts as a lever to multiply the force at the apex of the cut. At ordinary or room temperatures, GR-S treads have a tensile strength about 60 per cent of that of similarly reinforced natural rubber treads, but a flex-life rating of only about 10 per cent. The relaxation-failure effect is thus the equivalent of a 6 to 1 leverage. These factors, coupled with the higher heat build-up of GR-S under flexures of small amplitude and its high negative coefficient of tensile strength, all contribute to the acceleration of cut-growth.

At overcures the relative stiffness of the flexed GR-S is again pronounced, and is accompanied by a serious drop in breaking tensile and elongation, so the bad flex performance of overcured GR-S is understandable.

In 1934 Busse[11] considered "the tearing of an ideal, highly elastic medium that remains isotropic when stretched. . . ." For this ideal elastic ". . . if any force F applied to the grips is great enough to start a tear, it is more than

enough to make it continue across the sample. However, this is not true in general with rubber." In illustrating the differences in strain distribution of pure-gum Hevea samples, when they were cut before and after stretching, it is shown that, due to relaxation, the stresses in the stretched and relaxed sample do not build up to a maximum at the cut as they do in the unrelaxed sample, but are substantially equal to that prevailing across the uncut portion of the sample.

By analogy GR-S thus approximates the ideal elastic described by Busse more nearly than does natural rubber in the region of strain antecedent to tear on rupture, *i.e.*, it is more elastic at high elongations.

This inversion of elasticity of GR-S presents a unique challenge to the polymer chemist who has made it and to the rubber technologist who must compound it. Its hysteresis at low elongations must be reduced so that tires will run cooler, but at the same time its hysteresis at higher elongations must be increased so that it will relax under these higher amplitude flexures and so prevent premature flex-cut failure.

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OBSERVATIONS ON THE X-RAY STRUCTURE OF RUBBER AND THE SIZE AND SHAPE OF RUBBER CRYSTALLITES *

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INTRODUCTION

In former times, we used to be painfully aware of the shortcomings and elastic imperfections of Hevea rubber. With its disappearance, we have come to think of it as having an ideal balance in physical properties for a rubberlike material which it has been difficult to approach with synthetic polymers. For this reason, it is still important to investigate the molecular structure of Hevea rubber and to try to understand the characteristics of this structure which are responsible for its physical properties.

X-Ray diffraction methods can be applied to the problem of the molecular structure of Hevea rubber and a few synthetic rubbers, such as Butyl rubber and Neoprene, because crystallization occurs upon stretching. A detailed description of the x-ray diffraction results with rubber is available in a review article[1] and need not be repeated here. It should be pointed out that the story obtained from the x-ray structure is not complete because there are important aspects of the structure which are not revealed by this means. It is not possible to measure directly the length of the chain molecules. The nature of the amorphous phase, such as the system of cross-linking of the long chain molecules on vulcanization, does not become evident in x-ray patterns. The physical properties of Hevea rubber must depend on a delicate balance of primary and secondary valence forces. The x-ray method does not permit any direct measurement of these forces but merely shows the geometrical arrangement which results from the molecular forces.

Even with these limitations, much valuable information can be secured on the nature of the molecular rearrangements which occur upon stretching. Deductions can be drawn from the x-ray diffraction results regarding the form and spatial relationships of the long chain polymeric molecules and the manner in which they interact under stress. Correlations can then be looked for between the crystallization and the physical properties.

THE STRUCTURE REVEALED BY X-RAY DIFFRACTION

The x-ray diffraction pattern for stretched rubber, Figure 1, shows that small ordered regions or crystallites come into being upon stretching. There is a coexistence of an amorphous and a crystalline phase. The crystallites are aligned in the direction of stretching. Once a crystallite is formed, it does not undergo any appreciable deformation upon further stretching of the rubber. The crystallites serve as points of anchorage and reënforcement for the amorphous phase which continues to stretch and act as we think rubber should.

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They are analogous to pigment or filler particles. Their effect on the stress-strain curve would be expected to be similar. Figure 2 is given to illustrate the stress-strain curves of a gum stock, where the reënforcement is due solely to rubber crystallites formed at higher elongations, and a tread stock reënforced with carbon black as well. The rapid rise of the curve for the gum stock at

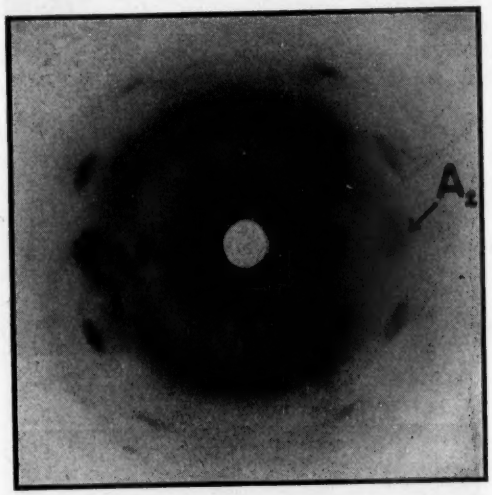

FIG. 1.—Stretched rubber; unvulcanized.

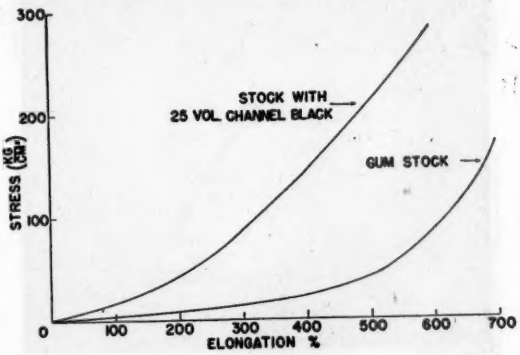

FIG. 2.—Effect of a reënforcing filler on the stress-strain curve.

higher elongations is due to the formation of crystallites. It should be stated that x-ray patterns show a unique difference in the structure of a stock reenforced with foreign particles and one reënforced with rubber crystallites alone. A foreign particle distorts the lines of stress so that the rubber crystallites which are formed are not aligned so well in the direction of stretch[2]. This is shown by the fact that the diffraction spots are drawn out into arcs in the pattern of Figure 3. When a rubber crystallite is formed in a gum stock, it does not interfere with the alignment of crystallites which are formed subsequently.

The physical properties of Hevea rubber are to be interpreted in the light of this remarkable ability for forming reënforcing crystallites and automatically

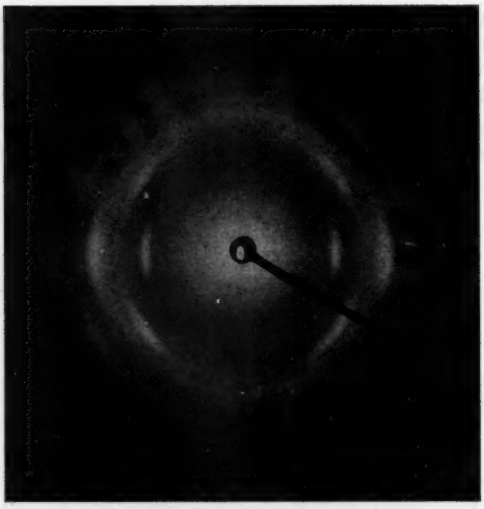

FIG. 3.—Stretched rubber; vulcanized; gas black loading.

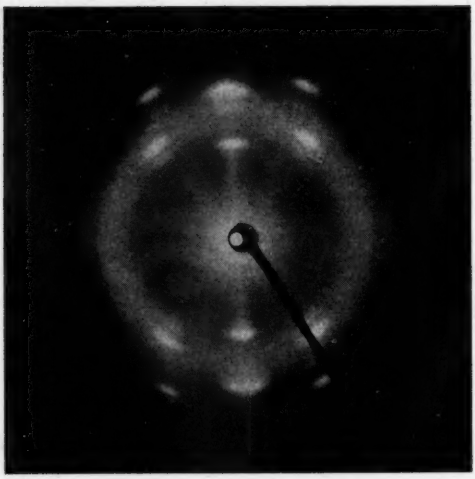

FIG. 4.—Unvulcanized rubber; 400 per cent elongation.
Molecular weight: 150,000.

adjusting its strength to the stress. For small deformations it can be soft, yielding, and rubberlike, yet, when higher stresses are applied it, so to speak, it summons its strength to resist them and becomes hard, tough, and tear-resistant.

It is well known that the reënforcing action of fillers depend on the particle size and shape. It seemed worthwhile, therefore, to see what information could be obtained from the x-ray diffraction patterns in regard to the size and shape of rubber crystallites in vulcanized rubber, especially since this is probably the only method available for such determinations.

It is now generally considered that the size of the crystallites has no relationship to the length of the chain molecules. They are formed by relatively short segments of adjacent long chain molecules, which are aligned parallel to each other in the direction of the fiber axis. There is still some uncertainty in regard to the lattice structure[1]. In the most recent determination, Bunn[3] arrived at a monoclinic unit cell with $a = 12.46$, $b = 8.89$, and $c = 8.10$Å.U. (fiber period), $\beta = 92°$. Four long chain molecules pass through this cell, parallel to the fiber axis. This is essentially the same as an orthorhombic cell suggested by Morss[4], except for the slight inclination of the fiber axis.

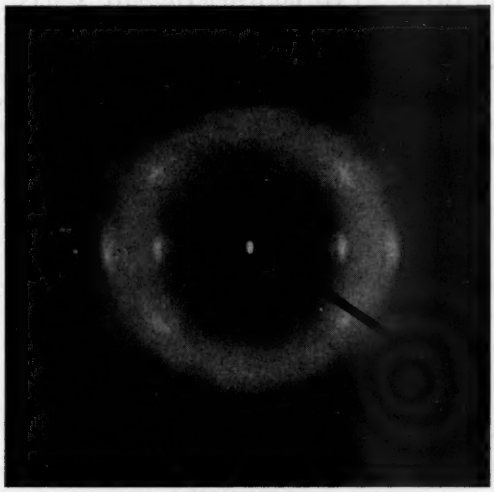

FIG. 5.—Unvulcanized rubber; 500 per cent elongation. Molecular weight: 125,000.

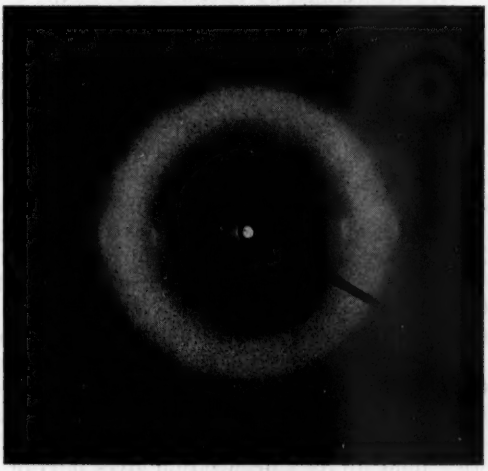

FIG. 6.—Unvulcanized rubber; 500 per cent elongation. Molecular weight: 90,000.

Morss, however, preferred a monoclinic cell with $a = 26.3$, $b = 8.15$ (fiber period), $c = 8.9$Å.U., $\beta = 109.5°$. Here the fiber axis is perpendicular to the plane of the other two and β is the angle between the a and c directions. The real differences between these three cells are very slight. For the purposes of this work on crystal size determination, there will be sufficient accuracy in regarding the two strong equatorial spots, designated as A_1 and A_2 in Figure 1, as arising from families of planes which are essentially perpendicular to each other as in the orthorhombic cell proposed by Mark and von Susich[5], for which $a = 12.3$, $b = 8.3$, and $c = 8.1$Å.U. (fiber period).

EFFECT OF MOLECULAR WEIGHT ON THE X-RAY PATTERN

Figures 4–6 are included to illustrate the lack of dependence of the crystallite size, as determined by the width of the diffraction spots, on the molecular chain length. The patterns were taken at room temperature. Here samples of rubber of different molecular weights were secured by progressively reducing the molecular weight of smoked sheet by mastication on a rubber mill. The

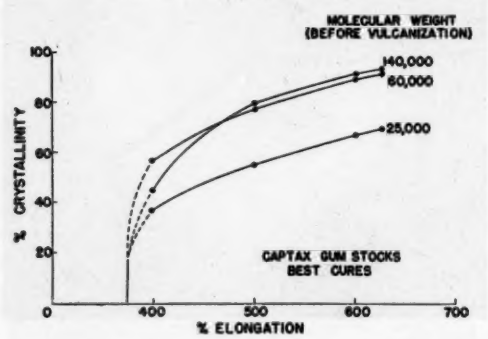

FIG. 7.—Dependence of crystallinity of vulcanized rubber on molecular weight.

molecular weights were determined by measurement of the viscosities of dilute solutions[6]. The number of crystallites formed upon stretching, as judged from the intensity of the diffraction spots, diminishes as the molecular weight decreases. There is no noticeable change in the size of the crystallites, judged from the diffuseness of the spots. Rubber composed of short chain length molecules apparently loses the property of forming crystallites upon stretching. This is probably connected with the greater thermal mobility of shorter chain molecules. Correspondingly, the rubber becomes soft and plastic. If low molecular-weight rubber is vulcanized, it regains to an inferior degree the ability to form crystallites upon stretching. Curves showing this are reproduced in Figure 7. The crystallinity was determined at room temperature by the method described by Field[7]. If the molecular weight of rubber is much less than about 45,000, it gives vulcanizates with low ultimate elongations and inferior tensile strengths. Such rubber, before vulcanization, is viscous and sticky. Rubber of high molecular weight has more structure before vulcanization which is retained, and influences beneficially the rubberlike properties. The physical properties of the low molecular-weight rubber are too much dependent on the cross-linkages formed during vulcanization. Such a highly cross-linked structure built up by vulcanization gives inferior physical properties compared to one composed of longer molecules with fewer cross-links and more crystallites.

METHOD OF DETERMINING THE SIZE OF THE CRYSTALLITES

Hengstenberg and Mark[8] made an x-ray determination of the crystallite size in stretched unvulcanized rubber, using the Laue method. The dimensions arrived at were 180Å.U. in the direction normal to the 020 planes, 530Å.U. normal to the 200 planes, and >600Å.U. in the direction of the fiber axis. The indices correspond to the cell of Mark and von Susich previously described.

These values indicate that the crystallite size is so large as to be on the borderline of sizes accessible to measurement by the x-ray method. This is generally considered to be about 1000Å.U. Due to this experimental handicap, it can be anticipated that variations in size and shape will be perceptible principally by measurements of the A_2 spot. The dimension in the direction of the fiber axis is particularly difficult to determine because the 002 spot is weak and is superposed on the amorphous halo. No determinations were made of this dimension in this work.

Under the best of circumstances, x-ray methods of particle size determination leave much to be desired in regard to precision. Cameron and Patterson[9] have reviewed the various methods available, tabulated the many sources of possible error, and evaluated the results which can be obtained. More recently Jones[10] and Taylor[11] have devised improved methods for correcting for the experimental conditions.

The Scherrer formula relating the particle size to the diffraction broadening is:

$$\beta = C\lambda/\epsilon \cos\theta. \tag{1}$$

β = angular broadening of the line (radians), ϵ = edge length of crystallite, λ = wave-length of x-rays, θ = Bragg diffraction angle, and C = a constant.

The value of C varies from 0.94 to 0.89, depending on the method of derivation of the formula. It can be taken as equal to unity with error negligible compared to other unavoidable uncertainties in the method (10).

The proper use of Equation (1) is hedged about with numerous restrictions, both experimental and theoretical. Originally, it was derived for parallel, monochromatic radiation, a point specimen and cubic crystals of cubic form in random orientation. For this work with rubber crystallites, the requirement for random orientation can be waived in view of a later, more general derivation by Bragg[9]. Work by Seljakow[12], Brill[13] and Laue[14] indicates that the equation can be applied in a very simple way to determine the particle shape for crystals of the orthorhombic system. If β is ascertained for the diffraction from planes $h00$, $0k0$, and $00l$, it gives, respectively, the extension of the crystallites in the directions normal to these diffracting families of planes. In view of the uncertainty in the determination of the unit cell for rubber, the approximation involved in considering it to be orthorhombic appears to be sufficiently accurate for the present work.

Scherrer defined the broadening β by the equation:

$$\beta_s = B - b. \tag{2}$$

B is the width, in radians, of the diffraction line at half-maximum density and b is a constant which depends on the experimental conditions. The use of a simple additive correction b is now generally regarded as incorrect. Jones[10] has described a method of mixtures for correcting the results for the experimental conditions during the exposure. His work is based on the integral line breadth defined by Laue as $\int I dx/I_{max}$. Here $\int I dx$ represents the total

intensity of the line and I_{max} is the maximum intensity. The integral breadth is the breadth of a uniform line having the same maximum intensity and the same total intensity as the actual line. This definition of line width is preferable to the "half-value width" because it gives more consideration to the broadening of the base of the peak by the smallest crystallites present. Jones mixed with the material under investigation a standard material of particle size sufficiently large to be considered infinite. For these particles, the breadths of the lines depend exclusively on the experimental conditions, since there is no broadening due to diffraction. They were called s lines. The lines from the material being studied were designated as m lines. The intensity distribution for an s line was written as:

$$I_s(x) = I_{s(max)}f(x) \tag{3}$$

To secure the m lines, it was considered that each element of width dx of an s line is broadened by diffraction into a line of the same area with intensity distribution:

$$I_d = I_{d(max)}F(kx) \tag{4}$$

These broadened elements combine to build up the m diffraction lines. k is a parameter which varies with the particle size.

Following through this concept, Jones showed that:

$$\frac{\text{true diffraction breadth}}{\text{observed breadth of } m \text{ line}} = \frac{\beta}{B} = \frac{\int F(kx)f(x)dx}{\int f(x)dx} \tag{5}$$

$$\frac{\text{breadth of } s \text{ line}}{\text{observed breadth of } m \text{ line}} = \frac{b}{B} = \frac{\int F(kx)f(x)dx}{\int F(kx)dx} \tag{6}$$

$f(x)$ can be determined experimentally, but intensity distribution functions must be assumed for $F(kx)$.

Using functions assumed by Laue:

$$F(kx) = \exp(-k^2x^2) \tag{7}$$

$$F(kx) = 1/(1 + k^2x^2) \tag{8}$$

and by Bragg:

$$F(kx) = \sin^2 kx/(kx)^2 \tag{9}$$

Jones plotted β/B against b/B and secured correction curves from which β could be obtained if b and B were measured experimentally.

Warren and Biscoe[15] gave the relation:

$$\beta_w^2 = B^2 - b^2 \tag{10}$$

Taylor[11] showed that Equation (10) corresponded to Jones' correction curve if $F(kx)$ was taken as $\exp(-k^2x^2)$. If $F(kx)$ is taken as $1/(1 + k^2x^2)$, a more moderate correction to the Scherrer relation is obtained. Taylor showed

that essentially this same result could be secured by taking β as the root mean between the Scherrer value and the Warren value, *viz.*:

$$\beta_T = [(B^2 - b^2)^{\frac{1}{2}}(B - b)]^{\frac{1}{2}} \qquad (11)$$

This value for β appeared to agree best with the experimental results, and seemed to take into some account the size-distribution factor. It therefore appears to be the preferred value for β for calculations of particle size where the value for b is available by calibration with a material with particle size large enough to be considered infinite.

RUBBER COMPOSITIONS USED

To determine whether or not significant variations occur in the size and shape of the crystallites in different rubber vulcanizates, a series of gum stocks was prepared, using diverse curing systems. By this means, a wide range in physical properties was secured.

Table I gives the recipes for the compounds, in parts by weight of the various ingredients.

Test data for the cures used are given in Table II.

TABLE I

Compound	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Smoked sheet	100	100	100	100	100	100	100	100
Zinc oxide		5	1	5	5	2		5
Sulfur	11	11	3	3	3	2		3
Stearic acid		1	0.5					
2-Mercaptobenzothiazole		0.4	0.5		0.25			
Piperidinium pentamethylene-dithiocarbamate						2		
Diphenylguanidine				0.5	0.25			
Dinitrobenzene							10	
Lead oxide							10	
Calcium oxide								10

TABLE II

Compound	Cure (min./° F)	Ultimate tensile strength (kg./sq. cm.)	Final elongation (%)	Stress at different elongations (kg./sq. cm.) 100%	300%	500%	700%	Combined sulfur (%)
A	240/285	150	815	5.27	13	26	70	4.00
C	30/260	125	815		10	18	60	1.20
D	40/285	148	760	3.25	12	28	105	1.20
E	20/260	220	790	3.3	14	33	134	1.20
F	5/260	129	735		10	26	104	.70
F	15/260	226	670		22	68		2.05
G	20/285	54	740	3.16	9	18	45	
H	80/285	97	825	4.57	11	20	53	2.20

EXPERIMENTAL PROCEDURE

The x-ray patterns were taken with a General Electric x-ray diffraction unit, using a copper target tube operated at 35-kv peak and 25 milliamperes. A filter of nickel foil (0.00Z-inch gauge) was placed over the film to reduce background and remove the Cu K_β radiation. A circular camera was used. It was equipped with a pinhole system as required for the Scherrer method. The radius of the camera was 70.9 mm. The rubber samples were supplied in the form of sheets the gauge of which was 2 mm. Narrow strips were cut from the

sheets, stretched, and mounted on the axis of the camera. To secure a measure of the line broadening b due to the experimental conditions, graphite, of particle diameter about 2 microns, was mixed with a dilute solution of glue and formed into a strip of the same gauge as the stretched rubber samples. This was mounted and the x-ray pattern secured in the same way as for the rubber samples.

Typical patterns, for compound *C* and compound *F*, are shown in Figures 8 and 9, respectively. All of the patterns were secured at high elongations so as to reduce the background due to the amorphous halo.

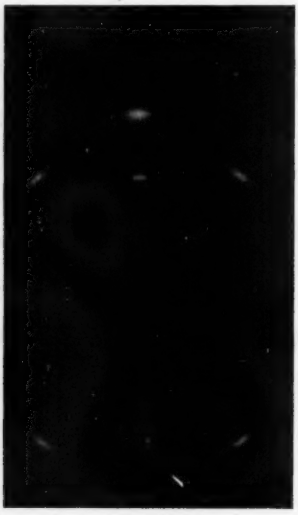

FIG. 8.—Compound *C*.

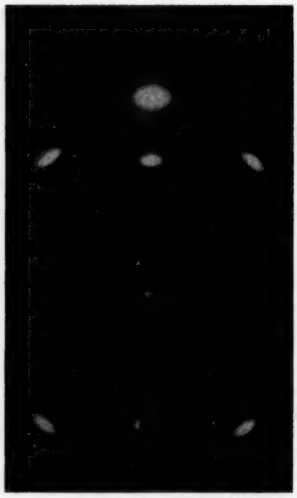

FIG. 9.—Compound *F*.

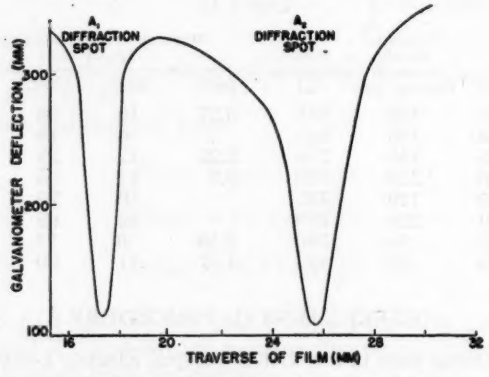

FIG. 10.—Microphotometer curve (Compound *C*).

The patterns were measured with a nonrecording microphotometer. The curves secured for stocks *C* and *F* are reproduced in Figures 10 and 11, respectively. It is apparent from these curves that it is difficult to determine the proper background deflection for calculating the photometric density of the A_2

spot because the spot lies on the edge of the amorphous halo. To overcome this difficulty, a background line was drawn from the outer edge of the A_1 spot, where the halo intensity is negligible, to the outer edge of the A_2 spot.

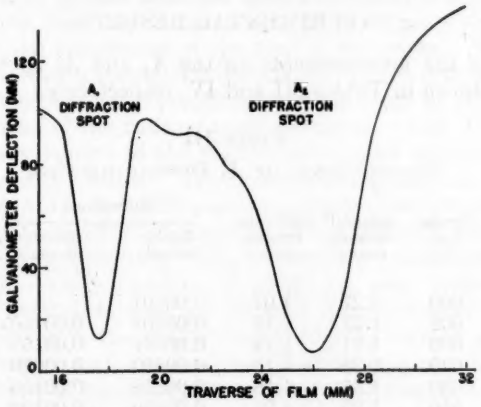

FIG. 11.—Microphotometer curve (Compound *F*).

Densities were then calculated for the outer half of the A_2 spot, where there is no appreciable halo background. The intensity distribution was then assumed to be symmetrical on both sides of the maximum. The density curves are shown in Figures 12 and 13. Areas under the peaks were measured to

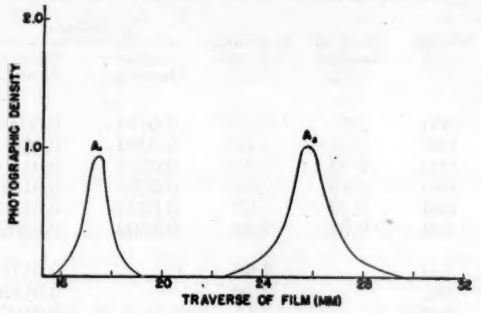

FIG. 12.—Intensity distribution curves (Compound *C*).

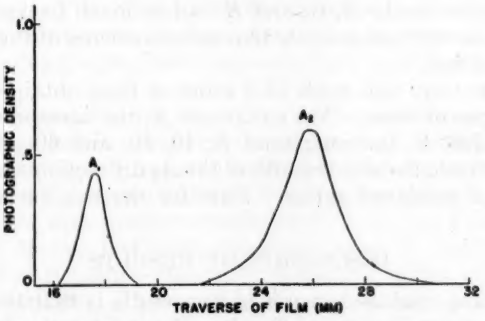

FIG. 13.—Intensity distribution curves (Compound *F*).

secure B, the integral breadth. For the graphite standard used for calibration, the integral breadth b of the 002 line, spacing 3.37A, was determined to be 1.08 mm. The half-value breadth was 1.07 mm.

EXPERIMENTAL RESULTS

The results of the measurements on the A_1 and A_2 spots for the various compounds are shown in Tables III and IV, respectively.

TABLE III

MEASUREMENTS OF A_1 DIFFRACTION SPOT

Compound	Elongation (%)	Integral breadth (mm.)	Half-value breadth (mm.)	β (radians) Taylor formula	β (radians) Scherrer formula	Crystallite dimension, A from β_T	Crystallite dimension, A from β_S
Evaporated latex	600	1.27	1.07	0.00501	—	310	>1000
C	600	1.27	1.18	0.00501	0.00155	310	1000
D	600	1.31	1.18	0.00581	0.00155	268	1000
E	600	1.25	1.12	0.00460	0.00070	338	>1000
F(5/260)	600	1.35	1.18	0.00658	0.00155	233	1000
F(15/260)	550	1.25	1.21	0.00460	0.00198	338	785
A	550		1.06		−0.00014		>1000
G	600		1.10		0.00042		>1000
H	600		1.05		−0.00028		>1000

TABLE IV

MEASUREMENTS OF A_2 DIFFRACTION SPOT

Compound	Elongation (%)	Integral breadth (mm.)	Half-value breadth (mm.)	β (radians) Taylor formula	β (radians) Scherrer formula	Crystallite dimension, A from β_T	Crystallite dimension, A from β_S
Evaporated latex	600	2.11	1.66	0.0194	0.0083	81	189
C	600	2.22	1.70	0.0292	0.0089	75	177
D	600	2.34	1.85	0.0329	0.0110	69	143
E	600	2.78	2.02	0.0295	0.0134	54	117
F(5/260)	600	2.42	1.87	0.0240	0.0113	65	139
F(15/260)	550	2.84	2.50	0.0302	0.0202	52	78
A	550		2.30		0.0173		91
G	600		2.10		0.0145		108
H	600		2.45		0.0195		81

The patterns for stocks A, G, and H had so much background relative to the intensity of the diffraction spots that measurements of the integral breadth did not seem justified.

Measurements were also made of a series of films obtained for compounds A and B at a series of cures. For compound A, the cures were 10, 30, 60, and 120 minutes at 298° F; for compound B, 10, 30, and 60 minutes at 260° F. Figure 14 shows the half-value breadth of the A_2 diffraction spot plotted against the percentage of combined sulfur. Data for the two cures of stock F also are plotted.

DISCUSSION OF RESULTS

One of the most obvious features of the results is that the crystallite sizes determined with β_T are much smaller than those determined with β_S. There

are two factors involved in this result. For the same width of spot, the Taylor procedure leads to the deduction of smaller crystallite sizes but, in addition, for the rubber diffraction spots the integral breadth used in the Taylor procedure is considerably greater than the half-value breadth used in the Scherrer equation. The fact that the integral breadth is larger than the half-value breadth is due to the broadening of the base of the peaks. This in turn is to be attributed to a heterogeneous size distribution of the crystallites and a considerable proportion of small crystallites. Such a state of affairs is consistent with the unsharpness of the melting point of rubber, which Alfrey and Mark[16] have suggested may be due to the mutual interaction and interference of the crystallites as they are formed. The decrease in entropy of a molecular segment which enters into a crystallite becomes progressively greater as crystallization proceeds, due to an effective decrease in the mobility and disorder of the amorphous connecting structure. This mechanism would lead to an unsharp melting point. In this connection, it would be very interesting to obtain measurements of crystallite sizes at different elongations to see if there is a progressive diminution in the size of the crystallites formed as the elongation increases. This experiment was not carried out because of difficulty in securing precise measurements of the integral breadth at low elongations in the presence of a strong amorphous halo.

Some correlation appears to exist between the crystallite dimension in the direction normal to the A_2 planes, the stress in the stretched rubber, and the percentage of crystalline material present. This is shown by the data in Table V.

TABLE V

Compound	Elongation (%)	Crystallite dimension, A	% Crystalline material	Stress (kg./sq. cm.)	Tensile strength (kg./sq. cm.)	Ultimate elongation (%)
C	600	75	68	33	125	815
D	600	69	71	52	148	760
E	600	54	75	60	220	790
F	550	52	85	87	226	670

The percentage of crystalline material in these stocks was determined by Field[7].

Table V shows the existence of definite trends. When a high percentage of crystalline material is present, the crystallites are smaller and the stress for a given elongation is higher. In the direction normal to the A_1 planes, differences in crystallite size are not so apparent. This may be real or it may simply be a result which is due to the fact that the x-ray method is insensitive for larger particle dimensions. The independent contributions of smaller crystallite size and increased crystallinity to the higher modulus cannot be determined from these data. Experience with fillers has shown that both factors would raise the modulus.

The curves in Figure 14 show that, for a given rubber composition, there is a definite correlation between the amount of combined sulfur and the width of the A_2 diffraction spot and, consequently, the size of the crystallites. The relative positions of the curves indicate that a given percentage of combined sulfur is concomitant with smaller crystallites in compound *F* than in compound *C*. It is difficult to say just what the significance of this is, but evidently irregularities in the structure caused by combined sulfur interfere with the growth of the crystallites. The question should be raised as to whether or not the widening of the spots is due to lattice distortion[17] by combined sulfur or

other cross-linkages or to internal microstresses such as those assumed for cold-worked metals[18]. This seems improbable for several reasons. The amount of combined sulfur and cross-linking is small. The A_1 diffraction spot does not give any evidence of lattice distortion. It does not seem probable that a lattice

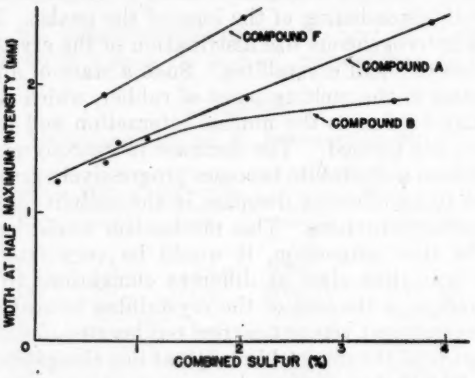

FIG. 14.—Effect of combined sulfur on half-value breadth of A_2 diffraction spot.

of this type would exhibit such a difference in the distortion in two principal directions. Furthermore, compound *G*, which does not contain any sulfur, shows an appreciable widening of the A_2 spot. Finally, one would not expect increased crystallinity, such as is observed, to be associated with lattice distortion. On the other hand, its association with smaller crystallites is very logical.

The insight into the structure of rubber which is to be gained by x-ray measurements of crystallite size seems well worthwhile, despite the rather severe limitations of the method.

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THE PHYSICAL CHEMISTRY OF RUBBER SOLUTIONS *

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The physicochemical behavior of rubber may conveniently be described in terms of two main factors, (1) its long-chain character, and (2) its chemical nature. It is frequently possible to neglect one of these; *e.g.*, Farmer and his coworkers[1] have shown that much light can be thrown on the organic chemistry of rubber from a study of structurally related, low-molecular hydrocarbons. In the following we shall, in the main, consider rubber as a typical member of the class of long-chain compounds, and much of this section is therefore of general application to linear high polymers.

THE MICELLAR THEORY OF RUBBER STRUCTURE

In view of this line of approach, it is natural to consider first the evidence for the size and shape of the rubber molecule. Two main points of view have been expressed. According to the first[2], rubber consists of molecules having a molecular weight of approximately 1000–1500, which in solid rubber are united in the form of "micelles". These larger units are supposed to have sufficient individuality to resist dispersion by most solvents, so that, *e.g.*, the osmotic pressure of a benzene solution measures the size, not of the molecule, but of the micelle. Only such solvents as camphor, menthol, and related substances are considered to break down the rubber to give a molecular dispersion. The alternative view[3] regards rubber as truly macromolecular, *i.e.*, made up of very long chains of isoprene molecules, polymerized into single molecules whose size, measured osmotically, is of the order of 100,000. A recent critical examination[4] seems to disprove the whole of the evidence advanced in support of the former view. The results of the earlier workers were shown to arise primarily from the rapid oxidative breakdown of rubber in molten camphor. When this is prevented by the exclusion of air, camphor behaves very similarly to benzene as a rubber solvent. The abnormally low molecular weights reported were obtained by the Rast method and are now shown to be merely indicative of the nonideal behavior which is characteristic of rubber solutions in general (see below). In default of any sound evidence for the micellar theory, we conclude therefore that rubber should be classed with the synthetic polymers as a macromolecule.

OSMOTIC PRESSURE MEASUREMENTS

The molecular weight of rubber may be determined by three methods: (1) ultracentrifugal, (2) osmotic, and (3) viscosimetric. Of these, (3) is not an absolute method, and (1) has been applied to a very limited extent, so that

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we must of necessity rely mainly on (2). Osmotic-pressure measurements of rubber solutions have been reported by a series of workers[5], whose results show considerable deviations in detail, but are in general agreement in finding molecular weights of the order of $1 - 4 \times 10^5$. The calculation of molecular weight from osmotic data is by no means straightforward, since the usual relationship between them is found not to hold. According to van't Hoff's law, the osmotic pressure Π is related to the molecular weight M of the solute and its concentration c by the equation:

$$\Pi = cRT/M \tag{1}$$

Experimentally it is found that Π/c is a function of c and the equation has, therefore, been used in the form:

$$M = RT \operatorname*{Lim}_{c \to 0} (c/\Pi) \tag{2}$$

Two difficulties are raised by this procedure: the experimental one of performing the extrapolation satisfactorily, and the need for some explanation of the departure from the simple law before any confidence can be placed in the results.

Ostwald[6] showed that the osmotic pressures of polymer solutions could be represented satisfactorily by an equation of the form:

$$\Pi = ac + bc^n \tag{3}$$

where a, b, and n are constants. He identified a with RT/M, which is equivalent to assuming Equation (2), and considered the first term as the true osmotic pressure. The second term, bc^n, in which n lay between 2 and 3, was regarded as a "swelling pressure", by analogy with the work of Posnjak[7], who had shown that if a piece of rubber was confined by a piston in a cylinder whose base, permeable to solvent, was immersed in solvent, the degree of swelling of the rubber was determined by the pressure applied to the piston. The pressure P corresponding to a given concentration c of rubber in the swollen mass was represented by an equation of the form:

$$P = bc^n \tag{4}$$

where the constants b and n were characteristic of the liquid, n lying usually between 2 and 3. Ostwald regarded the pressure measured by an osmometer as composite of an osmotic pressure and a swelling pressure. Although it will be shown later that this explanation must be rejected, Equation (3) has been widely used, especially by Carter and Record[8] and by Meyer and his coworkers[9]. The latter take $n = 2$, so that Π/c becomes a linear function of c.

An alternative explanation of the osmotic anomaly was proposed by Sackur[10] and applied to rubber by Meyer and Mark[11]. The dissolved particles were assumed to be solvated, so that the effective concentration of the solution was increased. Sackur took the volume of solvent removed in this way per gram of solute, to be independent of the solute concentration and wrote, instead of Equation (1):

$$\Pi = [c/(1 - cs)]RT/M \tag{5}$$

where s was a constant. Schulz[12] has further modified this equation by representing s as a function of Π by the equation:

$$\Pi s^{\nu} = k \tag{6}$$

which is again based on Posnjak's swelling-pressure Equation (4). Combination of (6) with (5) leads to:

$$M = cRT/\Pi\{1 - c(k/\Pi)^{1/\nu}\} \tag{7}$$

This equation has been employed very extensively by Schulz, and has been applied to rubber by Staudinger and Fischer[13]. Its use in extrapolating osmotic data requires the evaluation of the constants k and ν, which is done by the authors by a series of approximations. Where measurements are available for a series of M values, each Π/c–c curve is extrapolated roughly, and the resulting M inserted in Equation (5) to calculate s. The extrapolations are then adjusted until all the s values obey an equation of the form (6). A more direct method suggested by Gee[14] is to plot Π/c against $\sqrt{\Pi}$, which will be nearly linear if ν has the expected value of approximately 2. The degree of solvation required by this theory is very large (approximately 60 cc. per gram of rubber in a 1 per cent solution of rubber in benzene[15]), and cannot be held by any "chemical" bond. Even if we could regard this solvent as mechanically held by a spongelike molecule, Equation (6) cannot hold down to infinite dilution, for at this point $s \rightarrow \infty$. Both as a method of extrapolation and as an explanation of the osmotic behavior of solutions, this treatment must be regarded as thoroughly unsatisfactory.

An entirely different line of approach was suggested by Powell, Clark, and Eyring[16]. Pointing out that in many of its properties solid rubber behaves as if its molecules were composed of a large number of relatively short "segments", capable of more or less independent action, these authors apply the same idea to rubber solutions. Van't Hoff's law is assumed to hold, provided we use, in place of the actual number of rubber molecules present n_r, the "effective" number n_r^*. These are related to the volume fraction v_r of rubber in the solution and the molecular weight M_s of the segments of solid rubber by the empirical equation:

$$n_r^* = n_r[1 + (M/M_s - 1)v_r] \tag{8}$$

The present author can see no justification for the assumptions involved in writing this equation. By use of approximations valid for dilute solutions this leads to:

$$\Pi = RTc/M + RTc^2/\rho_r M_s \tag{9}$$

where ρ_r is the density of the rubber. This is evidently of the same form as (3), and has been employed by the authors to calculate values of M_s from the slope of the Π/c–c curve. Results obtained vary between 900 and 4500, and are considerably larger than the segment sizes deduced in other ways. Although this paper is of value in emphasizing that the rubber molecule may not be the effective unit in solution, we shall see later that a much more satisfactory explanation can be given of the varying slopes of the Π/c–c curves obtained in different solvents. [If (9) were valid these should, of course, all be equal.]

Before these theories can be further appraised, it is desirable to examine both the nature of osmotic pressure and the assumptions involved in the derivation of van't Hoff's equation. In considering the nature of the osmotic pressure of rubber solutions, it is necessary to abandon the kinetic picture frequently advanced of a pressure produced by the solute molecules bombarding the membrane. Guggenheim[17] has pointed out some of the difficulties associated with this view, and they are further enhanced if we compare the os-

motic pressure of a rubber solution with the swelling pressure of a rubber gel. Thermodynamically, these can both be defined as the hydrostatic pressure which has to be applied to the solution (or gel) to increase the vapor pressure of the solvent in the solution until it becomes equal to that of the pure solvent. Under these conditions the solution (or gel) is in osmotic equilibrium with the solvent, and it is obvious that osmotic pressure and swelling pressure are actually synonymous terms. Both are, in fact, to be understood, not as pressures exerted by the solute, but as pressures applied by the observer. Their physical origin may be regarded as the tendency of solvent molecules to flow from solvent to solution because of the increase of entropy which results. It can be shown that[18], for an ideal solution:

$$\Pi V_0 = T\Delta S_0 \tag{10}$$

where ΔS_0 = entropy of dilution and V_0 = molar volume of liquid.

In applying a pressure to the solution, we compress it slightly, reducing the mean intermolecular spacing, and producing (1) a decrease of entropy and (2) an increase of the energy content of the liquid. These factors combine to oppose the increase of entropy tending to cause osmosis, and at a certain pressure, osmotic equilibrium results. If α is the coefficient of thermal expansion of the liquid at constant pressure it may be shown[19] that the decrease of entropy is given by $\alpha V_0 P$ and the increase of energy by $V_0 P(1 - \alpha T)$. Since $\alpha \simeq 10^{-3}$ for organic liquids, the second term is generally the more important. This way of considering the problem emphasizes the fallacy involved in comparing a solution with a perfect gas, for which $\alpha = 1/T$, and the effect of pressure is solely to decrease the entropy. The increase of vapor pressure with applied hydrostatic pressure is also readily understood on this basis. It is easy to derive from it the thermodynamic relationship[20] between osmotic pressure and the vapor pressures of the solvent (p_0^o) and solution (p_0^m):

$$\Pi V_0 = RT \ln p_0^o/p_0^m \tag{11}$$

The theoretical basis of van't Hoff's law may be given in several ways. (1) The kinetic interpretation of osmotic pressure leads to it by analogy with gas pressure; rejection of this interpretation necessarily invalidates this line of argument. (2) If we assume Raoult's law to hold, we may replace p_0^m/p_0^o in Equation (11) by N_0, the mol.-fraction of solvent in the solution; for dilute solutions, the expansion $\ln N_0 \simeq 1 - N_0$ leads readily to van't Hoff's equation —this method merely exchanges one assumption for another which is in equal need of justification. (3) If the molecules of solvent and solute are regarded as approximately equal spheres, it can be shown statistically[21] that the entropy of dilution is given by $\Delta S_0 = -R \ln N_0$, which on substitution into Equation (10) gives the same result as above. This gives us a molecular basis for the law, and reveals at once the cause of its failure to apply to rubber solutions, for it is evident that the rubber molecule is not to be regarded as equal in size to the solvent molecule. The interpretation of the osmotic behavior of rubber solutions thus reduces to the statistical calculation of the entropy of dilution. Meyer[22] pointed out that this might be done approximately by computing the number of ways of arranging a long flexible chain on an array of lattice points. Each point may be occupied either by a solvent molecule or by a "segment" of the rubber chain, approximately equal in volume to the solvent molecule. The number of configurations possible is, of course, restricted by the fact that successive segments must occupy adjacent lattice points. Meyer's suggestion

was worked out independently by Flory[23] and Huggins[24], the entropy of mixing being calculated from the probability at a given concentration by means of Boltzmann's equation. Flory's result was:

$$\Delta S_0 = -(R/\beta)[\ln v_0 + (1 - 1/x)v_r] \tag{12}$$

where x is the number of segments in the rubber molecule; v_0 and v_r are the volume fractions of solvent and rubber; and β is the number of solvent molecules which are replaceable by one segment.

Both Meyer's original statement and Huggins's treatment assume $\beta = 1$. The latter's analysis leads to a similar result:

$$\Delta S_0 = -R[\ln v_0 + g_0(1 - 1/x)v_r] \tag{13}$$

where

$$g_0 = 1 + \sum_{i=1}^{\infty} \frac{1}{i}\left(\frac{2v_r}{Z'}\right)^{i-1} \tag{14}$$

and Z' is very nearly equal to the co-ordination number Z of the lattice. Direct calculation of the number of configurations is difficult for long-chain molecules, and an alternative method of approach has been used by Miller[25]. Improving on earlier analyses[26], he applied the Bethe approximation to evaluate the entropy of mixing of solvent molecules with "polymers" which could be regarded as made up of two or three units similar in size to the solvent. By a consideration of the way in which the results depended on the number of units it was possible to extrapolate to very long chains. Miller's final result[27] is:

$$\Delta S_0 = -R\left[\ln v_0 - \frac{Z}{2}\ln\left\{1 - \frac{2v_r}{Z}\left(1 - \frac{1}{x}\right)\right\}\right] \tag{15}$$

In the concentration range in which osmotic methods are applied, all three analyses lead to an equation of the form:

$$\Pi/c = RT/M + kc \tag{16}$$

k being given by $RT/2\beta\rho_r^2V_0$ (Flory and Huggins) or $RT(1/2 - 1/z)\rho_r^2V_0$ (Miller) where ρ_r is the density of the rubber. It is probable that these calculations of entropy can be refined, but even in their present state they provide a perfectly natural explanation for the departure of rubber solutions from van't Hoff's law. It is now clear that this law could not be expected to hold even in solutions in which the heat of dilution ΔH_0 is zero. When the heat of dilution is not zero, a further complication arises, for we have then[20]:

$$\Pi V_0 = T\Delta S_0 - \Delta H_0 \tag{17}$$

Few measurements have been made of the heat of dilution of rubber solutions, and none of sufficient accuracy to determine the form of the relationship between ΔH_0 and c. There is no reason, however, to expect this to differ from that found for mixtures of two liquids. Hildebrand[28] has shown that in the latter case ΔH_0 may be expressed as a power series in v_r, in which the first term involves v_r^2. Now, for dilute solutions $c \propto v_r$ and we may write:

$$\Delta H_0 = k_2c^2 + k_3c^3 + \tag{18}$$

Combination of (16) and (18) gives for the reduced osmotic pressure:

$$\Pi/c = RT/M + (k - k_2)c - k_3c^2 \qquad (19)$$

This equation will be seen to afford a justification for the use of Equation (2) for the calculation of molecular weights from osmotic data. It is important to notice that if the expression for ΔH_0 (18) had contained a term k_1c, the extrapolated value of Π/c would have been $RT/N - k_1$, which of course does not permit the use of Equation (2). Evidence in favor of the assumption $k_1 = 0$ is derived (1) from measured heats of mixing of simple liquids, and (2) from the fact that $\lim_{c\to 0}(\Pi/c)$ for polymers is independent of the nature of the solvent, in the few cases for which data are available[29].

The initial slope of the Π/c–c curve is given by (19) as $k - k_2$, where k_2 depends on the nature of the solvent. The slope, therefore, depends on the solvent, and it is evident that if a solvent can be found such that $k_2 = k$, it will form solutions which obey van't Hoff's law. Such solutions are, however, properly regarded as being less and not more "ideal" than those in which $k_2 = 0$.

We are now in a position to discuss the evaluation of molecular weights from the published osmotic data, and it is evident that the problem is essentially that of finding the best method of extrapolation. The difficulty becomes acute for high-molecular rubbers, since different methods of extrapolation, all equally consistent with the data, may lead to molecular weights differing by a factor of 2 or more[14]. Attempts to improve the extrapolation by measurements at higher dilution are of doubtful value on account of the increasing experimental error. The theoretical considerations given above support the method suggested by Meyer[9] of a linear extrapolation of Π/c–c. On the other hand, the most careful experimental work seems to be definitely opposed to this simple view. Gee and Treloar[20], by means of osmotic and vapor pressure data, have covered the whole range of concentration for the system rubber-benzene, and find a continuous curvature of the Π/c–c plot. A set of points covering a limited concentration range might, it is true, be considered collinear within experimental error, but both the slope and the extrapolated value depend on the particular set of points chosen. It does not, in fact, appear possible to find with certainty the limiting value of $(\Pi/c)_{c=0}$ from these measurements alone, at any rate in the case of the highest molecular-weight rubbers. A method of avoiding this difficulty was suggested by Gee[30]. By using a mixture of solvent and nonsolvent it is possible to increase ΔH_0 until the osmotic behavior of the solution approximates to van't Hoff's law at one temperature. For instance, rubber solutions in benzene +15 per cent methyl alcohol at 25° give values of Π/c almost independent of c from 8 to 20 grams per liter. This value of Π/c is considered to give the best available estimate of RT/M, and is consistent with the general curvature of the Π/c–c curves for rubber in benzene. A series of rubbers of different molecular weights were studied by Gee and Treloar, and their Π/c–c curves in benzene form a band whose width diminishes with increasing concentration until, at a concentration of approximately 80 grams per liter, the effect of molecular weight is indetectable. In Figure 1 the curves for the highest and lowest members of the series are plotted, together with some older data obtained by earlier workers[31]. The curves have been drawn through the latter points in such a way as to fit them into the general results of Gee and Treloar. Although the curves are consistent with

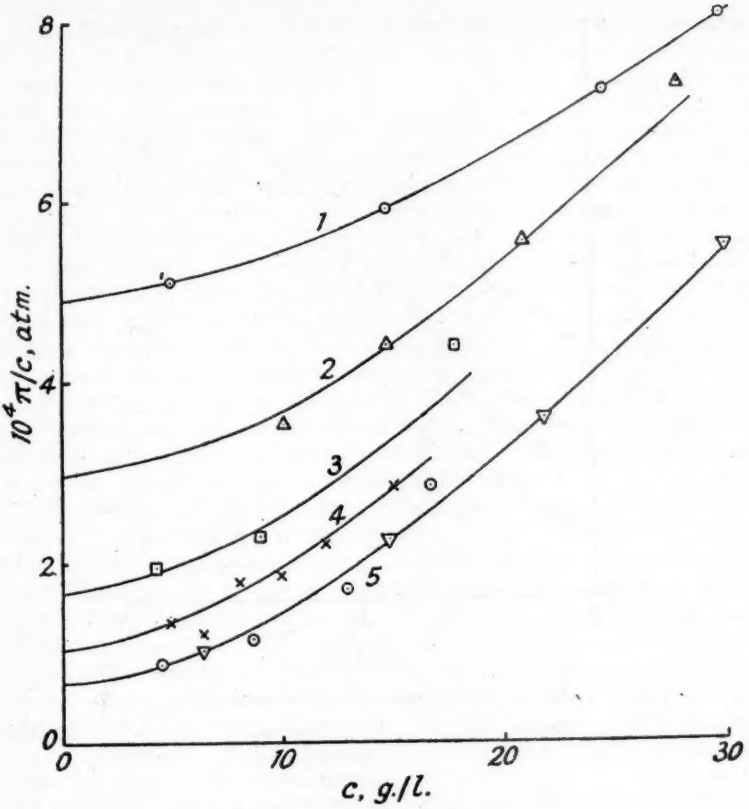

FIG. 1.—Osmotic pressure of rubber in benzene.

Curve	Symbol	Material	Reference
1	⊙	Thermally degraded rubber A	19
2	△	Fresh rubber	30
3	⊡	Crepe, alkali-treated	11
4	×	Ether sol	31
5	▽	Intermediate latex fraction	19
5	⊙	Crepe	

the data, it is obvious that they are not derivable from the data alone. A similar family of curves for toluene solutions of rubber has been constructed by combining the data of Meyer and Boissonnas[32] with those of Staudinger and Fischer[13], and is shown in Figure 2. Considered as a whole, Figure 2 is probably the best representation of the data, especially if the more complete results for benzene are taken as a guide. On the other hand, other extrapolations of any individual set of measurements are evidently possible. In Table I the molecular weights obtained from Figures 1 and 2 are compared with those calculated by the actual experimenters, whose methods of extrapolation are also recorded.

This review of the situation suggests that most of the published osmotic molecular weights of rubber may be subject to considerable uncertainty. The present author's opinion is that the above method of interpreting the data

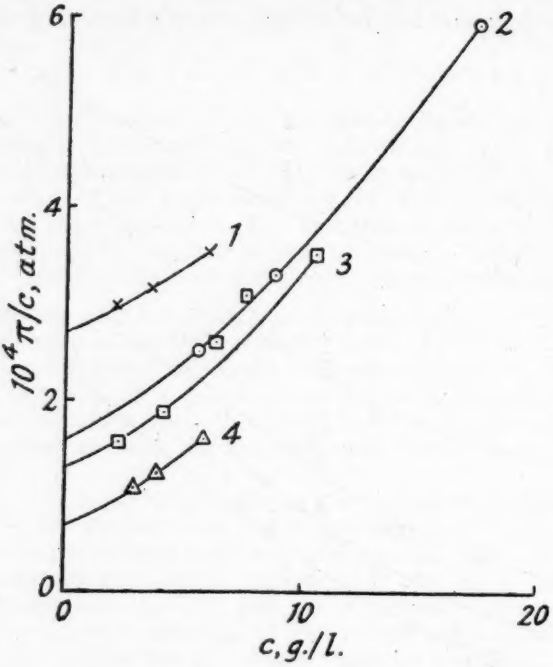

FIG. 2.—Osmotic pressure of rubber in toluene.

Curve	Symbol	Material	Reference
1	×	Purified rubber	5
2	⊙	Lightly milled crepe	32
3	⊡	Sol rubber	5
4	△	Al_2O_3-purified rubber	5

leads to the most probable molecular weights from existing data, and that, for future measurements, the best method is to find a solvent in which Π/c is independent of c over the working range. For rubber, such a solvent is benzene +15 per cent of methyl alcohol. It should be pointed out that this opinion is contrary to the views of other workers, of whom probably a majority favor linear extrapolation of Π/c–c[35].

TABLE I

Type of Rubber	Solvent	Reference	Extrapolation*	$10^{-5}M$ Authors' value	$10^{-5}M$ Figures 1 and 2
Raw crepe	PhH	11	1	3.6	*ca.*3
Crepe, alkali treated	PhH	11	1	1.5	1.5
Ether sol rubber	PhH	33	1	1.9	2.3
Fresh rubber	PhH	34	2	1.3†	0.8
Lightly milled crepe	PhMe	32	3	2.7	1.5
Rubber purified with Al_2O_3	PhMe	13	4	3.5	3.5
Sol rubber	PhMe	13	4	2.4_5	1.8_5
Rubber purified by Pummerer's method	PhMe	13	4	1.10	0.90

* Methods of extrapolation were: (1) Sackur's equation, (2) Ostwald's equation, (3) Ostwald's equation with $n = 2$, (4) Schulz's equation.
† Calculated by Ostwald[6].

If the Π/c–c plot is truly nonlinear, it appears to suggest that the calculated entropy of dilution is not quite accurate. Before we can be sure of this, it is necessary to have accurate data for the heat of dilution, and these are lacking. Several attempts have been made to estimate ΔH_0 from the temperature coefficient of osmotic pressure, but it has not hitherto been possible to obtain accurate data in this way. Meyer and Boissonnas[32] give data for toluene solutions which are consistent with the expression $\Delta H_0 = 20v_r^2$ cal. per mol., but the probable experimental error is ±50 per cent and the form of the equation is obviously indeterminate. Gee and Treloar[20] give for benzene solutions: $\Delta H_0 = 55v_r^2$, with a probable error of ±30 per cent. Earlier data of Kroepelin[36] lead to much larger heats, but are of extremely doubtful accuracy. All these workers agree in finding positive values of ΔH_0, and this is confirmed by direct calorimetric measurements of the integral heat of swelling[37]. The precise value found in this way depends somewhat on the history of the rubber sample, and is difficult to measure with precision, but values of the order of 2 cal. per gram of rubber were found in the case of benzene, with a smaller value (approximately 0.5 cal. per gram of rubber) for toluene. Chlorinated solvents gave an evolution of heat ($CHCl_3$, 3 cal. per gram; CCl_4, 2 cal. per gram). The only data covering a wide concentration range are those of Gee and Treloar[20] for benzene, calculated from vapor-pressure data. The accuracy is limited both by the smallness of the effect and by the relatively large correction for the nonideal behavior of benzene vapor[38]. The data are not satisfactorily represented by the simple quadratic equation, and a modified form was suggested, *viz.*, $\Delta H_0 = 156v_r^2/(1.7 - 0.7v_r)^2$. An alternative, based on (18), would be $\Delta H_0 = 55v_r^2 + 100v_r^3$. In Figure 3 the entropy of dilution for the rubber-benzene system is compared with the theoretical results of Flory and Miller, calculated from Equations (12) and (15). In each case one arbitrary constant has to be evaluated, and values of $\beta = 1$, $Z = 6$ have been selected in the following way:

For sufficiently small values of v_0, Equation (12) gives $\Delta S_0 \rightarrow -(R/\beta) \ln v_0$. Now, in this region, the vapor pressure is given[19] by $p_0^m/p_0^o = \alpha v_0$, where $\alpha = 4.4$ at 25°. This result requires that the limiting value of ΔS_0 shall be $-R \ln v_0$, whence $\beta = 1$. A better fit over the main part of the curve results from taking $\beta = 1.3$, but a complete fit would require β to be made an empirical function of v_0. Miller's Equation (15) gives $\Delta S_0 \rightarrow -R \ln v_0$ for all values of Z, and the value $Z = 6$ has, therefore, been chosen to fit the main part of the curve.

It is evident that either equation represents the main features of the curve extremely well, and confirms the essential correctness of the method of calculation. Since no specific assumptions have been made regarding the chemical nature of either the solvent or the polymer, the same entropy of dilution should be found for any other solvent-polymer system, provided only that the polymer molecule is sufficiently flexible to justify the assumption of very small segments. Experimental data by which this might be checked are lacking, and the best we can do is to compare values of $-\Delta G_0/T$ obtained from vapor-pressure data[39], with the theoretical curve for ΔS_0. Three such comparisons are included in Figure 3, and conform very closely to the expected behavior. If $\Delta H_0 > 0$, we have $-\Delta G_0/T < \Delta S_0$, and this is seen to be the case for toluene and acetone. The toluene curve is almost identical with the corresponding curve for benzene, and the larger displacement of the acetone curve agrees with the much greater heat of dilution to be anticipated. It is noteworthy that the

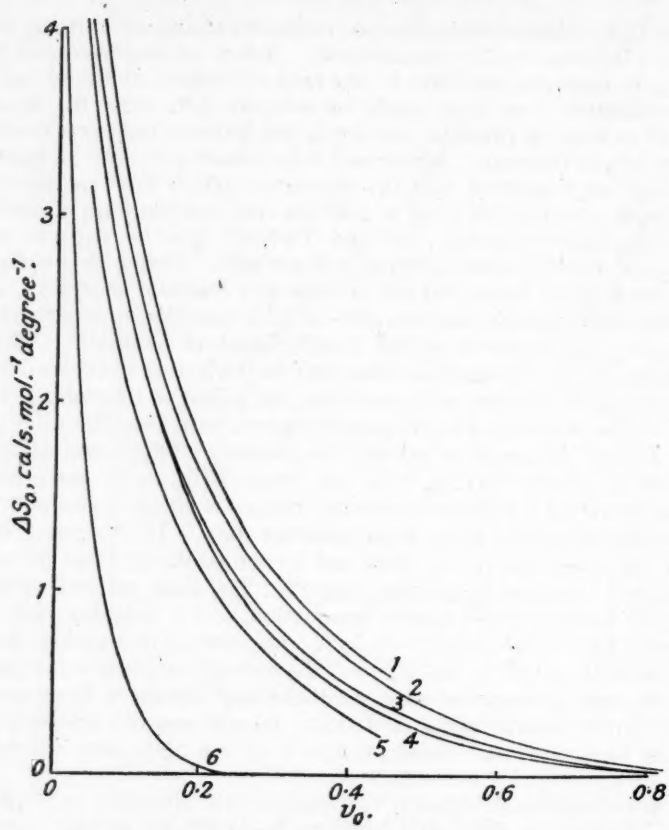

FIG. 3.—Entropy of dilution of rubber solutions.

Curve	Source	Reference
1	$-\Delta G_0/T$ for $CHCl_3$	41
2	Theoretical (Flory)	23
3	Theoretical (Miller)	27
4	Experimental: benzene	20
5	$-\Delta G_0/T$ for toluene	32
6	$-\Delta G_0/T$ for acetone	41

chloroform curve lies above the theoretical entropy curve: this is to be expected, since Hock and Schmidt[40] have shown that $\Delta H_0 < 0$.

On the assumption of an entropy of dilution given by one of the theoretical equations, it is possible to make considerable progress in understanding other properties of rubber solutions and gels. Before this work can be described, it is necessary to consider another method of investigating the size and shape of rubber molecules, *viz.*, the measurement of solution viscosities.

THE VISCOSITY OF RUBBER SOLUTIONS

It is not proposed to discuss at length the general problem of the viscosities of high-polymer solutions, since a number of recent articles have been devoted to this topic[42]. We shall be concerned with the problem only in so far as it bears on the determination of the size and shape of rubber molecules.

Two general methods have been adopted in discussing the viscosity of polymer solutions. The first treats the suspended particle (molecule) as a rigid ellipsoid, whose axial ratio is calculated from the experimental data[43]. This model is so far removed from our concept of the rubber molecule in solution that it does not seem profitable to discuss it further in this paper. The other method attempts to relate the viscosity of a dilute solution with the molecular weight of the solute. The possibility of doing so depends on the assumption of Staudinger's law, or some modification of it. As originally proposed[3], it took the form:

$$\eta_{sp.} = k_m c M \tag{20}$$

where $\eta_{sp.}$ is the specific viscosity of a solution of concentration c, and k_m is a constant. Since it is found that $\eta_{sp.}/c$ is always dependent on c, it is customary to employ the value extrapolated to infinite dilution. This quantity was termed by Lansing and Kraemer[44] the intrinsic viscosity $[\eta]$, and by Staudinger, Berger, and Fischer[45], as the viscosity number, Z_η. It has also been clearly recognized that $(1/c) \ln \eta_r$ is much less dependent on c than is $\eta_{sp.}/c$[46], so the most convenient form of equation is:

$$M = K \operatorname*{Lim}_{c \to 0} \left(\frac{1}{c} \ln \eta_r \right) = K[\eta] \tag{21}$$

where $\eta_r = 1 + \eta_{sp.}$ is the relative viscosity of the solution. Equation (21) might be justifiable in one of two ways: (1) by an acceptable theoretical derivation, or (2) by comparing intrinsic viscosities with molecular weights measured in other ways.

A very clear discussion of the factors involved in the shear of a liquid containing nonspherical particles is given by Lawrence[47]. Rigid elongated particles increase the viscosity of a solution when the two ends of a particle are situated in layers of the liquid which, as a result of sheer, are moving at different rates. There is a tendency to stretch the particle and to rotate it into the streamlines. Orientation is, however, upset by Brownian motion, and a certain mean orientation results from the interplay of these two forces. At high rates of shear, orientation becomes increasingly perfect, whereas a rise of temperature favors disorientation. Furthermore, it is evident that maximum disturbance of flow will occur when the particle lies directly across the streamlines, flow being quite undisturbed by thin particles if perfectly oriented. These considerations provide a ready explanation of Robinson's observations[48] on the viscosity of solutions of tobacco mosaic virus. The viscosity falls rapidly as the rate of shear is increased, and in a typical capillary viscometer of the Ostwald type it is much smaller than in a Couette viscometer, in which the rate of shear can be made very small.

The application of these ideas to rubber solutions requires us to know the form of the rubber molecule in solution. Tobacco mosaic virus is known to consist of rigid rods, but Staudinger's original suggestion[3] that all polymer molecules were similarly rigid has long been rejected. The chemical nature of rubber leads inevitably to the conclusion that the molecule must possess a high degree of freedom of rotation about the single bonds in its structure. As a result of this freedom, a fully extended configuration is extremely improbable, and in the absence of any restraining force the molecule assumes a series of constantly changing, randomly kinked forms, in which the average distance between its ends is far less than the maximum possible. A statistical analysis

of the most probable molecular configuration has been attempted by a number of workers[49], and an account of their work is given in a recent report[50]. It will suffice here to point out that all treatments, in addition to other approximations, involve the assumption that all configurations formed by rotations about a single bond are of equal energy.

Huggins[51] has attempted to calculate the viscosity of a solution of long-chain molecules along the following lines. The molecule is treated as a chain of "submolecules", whose distribution is given by equations analogous to those of Kuhn[49]. Each submolecule is, in general, moving with a velocity different from that of the layer of liquid with which it is in contact. This relative velocity is calculated, and the work done on the liquid by the submolecule estimated by means of Stokes's law. A summation over all the submolecules gives the total work done, and hence the contribution of the molecule to the viscosity of the solution.

The result of this calculation is to give a relationship between viscosity and molecular weight which, for long molecules, reduces to the form of Equation (21), a definite value being given to the constant K in terms of atomic parameters. This theoretical treatment is undoubtedly a great advance on any other attempt to solve the problem, and goes far to suggest that Staudinger's law should be approximately valid for rubber solutions. An evident source of error is the assumption that the molecular shape distribution will be unaffected by suspending the molecule in a liquid undergoing shear. Huggins has suggested that the correction is likely to be small, but a fuller analysis is desirable. Experimentally the problem could be largely solved by studying the viscosity of rubber solutions over a wide range of rates of shear. A more serious objection to this treatment is inherent in Kuhn's distribution function. Since the molecule is idealized to a series of points, the effect of molecular size is neglected, and the calculated distribution must be much more compact than the real one. It follows that Huggins's calculated viscosity must be too small, but provided that only the value of the constant K be thereby affected, the main conclusion of Huggins's analysis will still be valid.

Theory thus gives us reason to think that Equation (21) should be approximately valid, and most workers would agree that the experimental evidence leads to the same conclusion. The use of viscosities for molecular-weight determination is, however, only possible if Equation (21)—or some other—holds accurately. This can at present only be tested experimentally and, as we shall see, there is no consensus of opinion about the results. Before giving the experimental results, a number of other theoretical points must be mentioned.

In a rubber solution there exist molecules covering a range of molecular lengths, and the "molecular weight" of the rubber is, therefore, to be interpreted as a mean value. If we have n_i molecules of molecular weight M_i, the mean molecular weight $M_{\text{osm.}}$, as ordinarily understood, is given by:

$$M_{\text{osm.}} = \sum_i n_i M_i / \sum_i n_i$$

This equation is valid for molecular weights determined by the osmotic method, but it can be readily shown[44] that, if Staudinger's law holds for each component of a mixture, the mean viscosity molecular weight M_v of the mixture is given by:

$$M_v = \sum_i n_i M_i^2 / \sum n_i M_i$$

It is evident that $M_v > M_{osm.}$ and that the ratio $M_v/M_{osm.}$ is a measure of the degree of homogeneity of the rubber. There are two ways of avoiding this difficulty to test Equation (21). One is to compare viscosities with ultracentrifuge data, which can be employed to calculate M_v[44], the other is to fractionate rubber so as to obtain substances as homogeneous as possible, and then to compare the viscosity with the osmotic molecular weight.

A second difficulty arises from the possible existence of branches in the molecular chain of rubber. Although there is no evidence of this from other sources, it is difficult to point to any fact which conclusively disproves the possibility. Now, it is clear that, in general, a molecule possessing a branched structure takes up a more compact form than a truly linear molecule and, therefore, contributes less to the viscosity. It has, therefore, been suggested (see below) that viscosity measures the length of the main chain, and is comparable with the other molecular-weight methods only in the case of linear molecules. This argument is not very convincing, for, although it may be true that a short side chain contributes little to the intrinsic viscosity, yet the effect of the long side-chains, implied by the concept of branching, cannot be negligible. Qualitatively, however, it is clear that branching should reduce $[\eta]$, and therefore invalidate the method.

The last difficulty we shall discuss is the effect of solvent. The theory as formulated predicts that $[\eta]$ should be the same in all solvents, which is well known to be untrue. A satisfactory theory must give some explanation of this anomaly, and also suggest the best solvent for viscosity measurements. It seems probable that the different values of $[\eta]$ found in various solvents are to be associated with different forms taken up by the molecule in solution[52]. This would not be difficult to understand, for it is only in a solvent in which rubber forms ideal solutions ($\Delta H_0 = 0$) that the various possible configurations of the molecule can have equal energy. Now this is a primary assumption in calculating the entropy of solution, as described earlier. If $\Delta H_0 > 0$, the total energy of the system (rubber and liquid) is reduced by the molecules taking up more compact configurations, so as to reduce the interface: rubber/liquid. Despite the lower entropy of such a state, the net effect is a reduction of free energy. It is clear, therefore, that the larger ΔH_0 becomes, the more compact is the mean molecular configuration, and the lower the solution viscosity. If, on the other hand, $\Delta H_0 < 0$, extended configurations become favored, and solutions of high viscosity are to be expected. Although, as already noted, few values of ΔH_0 are available, we shall see later how they may be estimated, and the data are in general agreement with the prediction that $[\eta]$ should fall with ΔH_0. Since the theory is worked out for $\Delta H_0 = 0$, we have also a criterion for selecting the best solvent, though in a later section it will be shown that other conditions may in practice need to be considered.

The first experimental data to be considered are those in which intrinsic viscosity has been compared with osmotic molecular weight. The evaluation of this evidence depends to a considerable extent on the method employed in extrapolating the osmotic data, and it is clear that the same method must be applied to all the data. The figures given in Table II are based on the method described above, the actual extrapolations for toluene being shown in Figure 2. Values in parentheses are those given by the original authors, and the effect of different methods of extrapolation is only too evident.

On the basis of the data for the fractions, Gee[30] suggested that Staudinger's law holds for rubber within the accuracy (approximately 10 per cent) with which it can at present be tested, at any rate over the molecular weight range 60,000–

350,000. Subsequent work (see below) has led to the conclusion that these fractions were much less homogeneous than was thought at the time, so one might expect the ratio $M/[\eta] = 6.0 \times 10^4$ to be somewhat too low. On the other hand, the data available have now been considerably extended, and confirm the original conclusion that, for rubbers of high molecular weight, $[\eta] \propto M$, with a constant of proportionality close to that previously found.

TABLE II

COMPARISON OF INTRINSIC VISCOSITY WITH OSMOTIC MOLECULAR WEIGHT

Material	Viscosity solvent	Reference	$10^{-5}M_{osm.}$	$[\eta]$	$10^{-4}M/[\eta]$
(1) *Fractionated rubbers*					
Intermediate latex fraction	Benzene	30	3.5	5.8	6.0
Low latex fraction	Benzene	30	2.1	4.0	5.3
Hydrocarbon from oxide fraction	Benzene	30	0.66	1.02	6.5
(2) *Unfractionated rubbers*					
Crepe (acetone extracted)	Benzene	30	2.6	5.7_5	4.5
Sol rubber	Benzene	30	3.0	5.7_5	5.2
Sol rubber	Toluene	5	1.8_5 (2.4$_5$)	3.8	4.9 (6.4)
Purified with Al_2O_3	Toluene	5	3.6 (3.5)	8.4	4.3 (4.2)
Lightly milled crepe	Toluene	53	1.6 (2.7)	3.7	4.3 (7.3)

The ratio $M/[\eta]$ for unfractionated rubbers is seen from Table II to be somewhat lower than for the fractions, in agreement with their wider range of molecular weights. [It will be noted that if the published osmotic molecular weights are employed this last statement is untrue.]

The other possible way of testing the Staudinger law in the high-molecular region is by comparison of intrinsic viscosity with ultracentrifuge molecular weights, which may be done for any rubber, whether homogeneous or not. No systematic work has been done on these lines, but Kraemer[54] has reported the results given in Table III.

TABLE III

COMPARISON OF INTRINSIC VISCOSITY WITH ULTRACENTRIFUGE MOLECULAR

Substance	Viscosity solvent	$10^{-5}M$ (in ether)	$[\eta]$	$10^{-4}M/[\eta]$
Sol A	Ether	4.00	1.85	21.5
	Benzene	...	2.60	15.5
Sol B	Ether	4.35	2.05	21
	Benzene	...	3.74	11.5
Low-viscosity rubbers	Ether	0.69	0.34_2	20
	Chloroform	0.635	0.50_7	12.5

It is difficult to discuss these figures, since they were presented without experimental details beyond a statement that the sedimentation equilibrium method was employed. Considering the viscosity in ether, we find support for the Staudinger equation. The intrinsic viscosities measured in benzene are not accurately proportional to M, and the ratios of $M/[\eta]$ are approximately twice as high as those found from osmotic data. This discrepancy requires further investigation, but it is relevant to point out that the difficulty of reconciling osmotic and ultracentrifuge data is not confined to rubber. Signer and Gross[55] have used the sedimentation equilibrium method to estimate the molecular weights of some polystyrene fractions in chloroform, obtaining values which are proportional to $[\eta]$. They point out that the calculation requires the assumption of van't Hoff's law, and give the apparent molecular weight of one fraction ($M = 3 \times 10^5$) as a function of concentration. The

deviation from van't Hoff's law revealed by these figures may be expressed in terms of the calculated osmotic pressures. $10^4\Pi/c$ is found to rise from 0.73 at infinite dilution to 2.9 at a concentration of 2.5 grams per liter. Schulz[12] gives osmotic data for a polystyrene fraction in toluene, which show $10^4\Pi/c$ increasing, over the same concentration range, from 0.73 to 0.87. Although it is true that the slope of the Π/c–c curve is probably higher for chloroform than for toluene (ΔH_0 is probably negative for chloroform), yet there seems a definite discrepancy here. Almost the whole of the work on the ultracentrifuge has been carried out with aqueous solutions, and it is perhaps better to suspend judgment on the above results until more extensive experience has been gained of the technical difficulties encountered with nonaqueous solutions.

No other method is available for testing the applicability of Staudinger's equation to high-molecular rubbers, but if we assume its validity, the constant may be determined by reference to lower members of the series. By comparing intrinsic viscosities with molecular weights determined cryoscopically, we can test the equation for low-molecular rubbers and, if it proves valid in this region, employ the constant thus obtained for rubbers of much higher molecular weight, assuming the possibility of the enormous extrapolation involved. This is the method first employed by Staudinger and Bondy[56], and subsequently adopted and refined by Kemp and Peters[57]. The former workers used crude degradation products obtained by heating tetralin or xylene solutions of rubber in air; the latter started from similar substances, but subsequently fractionated them, obtaining in this way a range of products of low molecular weights, but containing various amounts of oxygen (up to nearly 6 per cent) and with rather low iodine values. Some of these substances became insoluble on heating in a vacuum to 100°, probably owing to a form of cross-linking or oxygen vulcanization. Since all their products were treated in the same way, there is a considerable assumption involved in regarding them simply as low-molecular homologs of rubber. Intrinsic viscosities in benzene were compared with cryoscopic molecular weights determined in benzene or cyclohexane. The calculated molecular weight was substantially independent of concentration for $M < 2000$, but for the higher fractions deviations occurred which are, of course, parallel to those found in the osmotic data. The authors reject all such results as "unreliable", but in view of our conclusion that extrapolation to infinite dilution leads to the correct molecular weight, there is evidently no basis for this selection. Table IV summarizes their results, molecular weights marked *

TABLE IV

COMPARISON OF INTRINSIC VISCOSITY IN BENZENE WITH CRYOSCOPIC MOLECULAR WEIGHT

Material	$10^{-5}M$	$[\eta]$	$10^{-4}M/[\eta]$
Squalene[58]	0.00410	0.023	1.8
Fraction 3	0.012	0.058	2.1
Acetone-soluble, washed with alcohol	0.014_2	0.065	2.2
Fraction 4	0.064*	0.198	3.2
Fraction 5	0.090*	0.262	3.4_5

having been obtained by extrapolation. Data are included for squalene, a hexamer of isoprene, of known constitution.

Considering only the lower fractions to be reliable, Kemp and Peters take $M/[\eta] = 2.2 \times 10^4$, which they then use in Equation (21) to calculate much higher molecular weights. The disagreement of the results with the osmotic data is ascribed to the errors in the latter. From the point of view set out in

the present paper, all the figures of Table IV are equally trustworthy. Since they reveal an obvious trend of $M/[\eta]$ with M, they must, in the opinion of the present author, lead to the conclusion that Staudinger's law does not hold accurately for low-molecular substances. This behavior is not confined to rubber, but has been found in all series of substances whose viscosities have been studied down to the low-molecular-weight region[59]. Several types of explanation have been proposed.

(1) Kemp and Peters reject cryoscopic and osmotic data for solutions which do not obey van't Hoff's law, and assume Staudinger's law to hold.

(2) Staudinger and Fischer[13] accept the ostmotic data as correct, but also assume the validity of the viscosity law, and derive a constant in the same way as Kemp and Peters. Where the latter leads to molecular weights lower than those measured osmotically, the material is assumed to be branched. Arguing that viscosity is a measure of molecular length, these authors define the degree of branching as $M_{osm.}/M_v$. Unless evidence of branching is forthcoming from other sources, it seems preferable to seek another explanation of the data.

(3) Most workers now accept the evidence at its face value, and thus conclude that Staudinger's law is not accurately obeyed, even by homogeneous, linear polymers. Two modifications of the equation have been suggested. Except for very low M, the data for the polyesters[55] obey an equation of the form:

$$M = K[\eta] + K' \tag{22}$$

A more radical modification has recently been proposed by Houwink[60]:

$$M = K[\eta]^n \tag{23}$$

Flory[61] has reported that this equation holds for polybutenes between $M = 5 \times 10^3$ and 5×10^5, giving $n = 1.65$. We may seek to apply these equations to rubber by combining the data of Tables II and IV. A fairly good fit is given by Equation (23), if we take $K = 4.2 \times 10^4$, $n = 1.23$, but the lowest of the osmotic points is badly out. Equation (22) is very little better than (21).

Summarizing, it is evident that the precise relationship between molecular weight and the intrinsic viscosity of rubber solutions over a wide range of M remains to be determined. The principal experimental difficulty to be overcome is that of obtaining rubbers of medium and low molecular weights which we can confidently assume to be linear and reasonably homogeneous. Until this can be done, the extension of the Staudinger equation beyond the molecular weight range 60,000–350,000 is dangerous. Within that range, the opinion of the present author is that Equation (21) may be applied to intrinsic viscosities measured in benzene solution, using $K = 6.0 \times 10^4$, and that the molecular weights thus obtained are probably accurate to within 10 or 20 per cent.

We now discuss the use of solvents other than benzene for the measurement of intrinsic viscosities. Gee[30] has presented data which show that, within the molecular weight range 60,000–350,000, the intrinsic viscosities in a number of solvents are accurately proportional; *i.e.*, if the Staudinger law is valid for benzene, it is valid also for any of the other solvents examined, provided that the appropriate constant be used for each. Kemp and Peters[62] have recently shown that this is by no means true over a wide range of molecular weights, in the case of polyisobutylene. For instance, with $M = 1000$, the intrinsic

viscosities in cyclohexane, carbon tetrachloride, hexane, chloroform, and benzene are in the ratios 127, 118, 100, 100, 85. With $M = 10^5$ these values become 140, 120, 100, 100, 38, the intermediate variation being nearly linear with log M. With $M < 1000$ very large changes occur in the ratios, and it is evident that if Staudinger's law holds in this region for hexane solutions (taken as standard by Kemp and Peters), it cannot also hold for the other solvents.

No explanation has been offered of the curious behavior of low-molecular rubbers in different solvents, though Burgers[43] has pointed out that the viscosities of solutions of some of the paraffins studied by Meyer and van der Wyk[63] are lower than those given by A. Einstein's equation for spherical molecules. The intrinsic viscosities of high-molecular rubbers are readily interpreted on the basis of the theory already discussed. Although the heats of mixing of rubber with various solvents are unknown, yet there is reason to believe (see below) that the degrees of swelling, Q, of a vulcanized rubber in a series of solvents run closely parallel with their heats of dilution. We should, therefore, expect the intrinsic viscosities of a sample of rubber to be a simple function of the degrees of swelling. In Table V some swelling data given by

TABLE V

INTRINSIC VISCOSITIES AND SWELLING POWER

Liquid	Q (cc. liquid per cc. rubber)	Relative intrinsic viscosities	
		Kemp and Peters	Gee
Carbon tetrachloride	5.0*	112	...
Chloroform	4.2*	107	...
Toluene	4.2	103	...
Benzene	3.9	(100)	(100)
Cyclohexane†	...	98	104
Amyl acetate	1.8	...	58
Ethyl ether	1.6	...	64
Hexane	1.2	88	...

* Unpublished data, quoted by kind permission of G. S. Whitby.
† Q not measured, but almost certainly occupying this position in the table (by comparison with swelling in other liquids).

Whitby, Evans, and Pasternach[64] are compared with intrinsic viscosities found by Kemp and Peters[57] and Gee[30].

The parallelism is evidently not exact, particularly in the case of the more polar liquids, but is sufficiently good to lend general support to the theory.

It was suggested earlier that the ideal viscosity solvent would be one for which $\Delta H_0 = 0$. Probably cyclohexane falls nearest to this condition, but is well known to disperse rubber with some difficulty (see below). Being a somewhat viscous liquid, it also leads to highly viscous solutions, which are evidently undesirable. Benzene lies next to cyclohexane in the table, and is a very satisfactory rubber solvent. It is, therefore, the first choice of the present author as the standard liquid for the determination of intrinsic viscosities of rubber solutions.

SOLUBILITY AND FRACTIONATION

Two main lines of attack on this problem may be distinguished: (1) an experimental study of the behavior of rubber towards various solvents, and (2) recent attempts to explain the main features of these results by a theoretical approach. It will be convenient in the present paper to reverse the historical

order, so as to be able to use the results of the calculations in discussing the significance of the experimental work.

Brønsted[65] was one of the first to suggest a plausible explanation of the unusual solubility relationships of high polymers. He argued that the distribution of large polymers between two phases would be determined almost entirely by the difference of potential energy between them. Assuming this to be proportional to the molecular weight of the polymer, he obtained for the relative concentrations c' and c'' of polymer in two phases in equilibrium:

$$\ln c'/c'' = \lambda M/RT \tag{24}$$

where λ is a constant, characteristic of the solvent and the series of polymers considered. If M is large, it is readily seen that the ratio c'/c'' may assume extreme values. Considering λ as continuously variable along a series of liquids, it is clear that, as λ decreases through zero and becomes negative, the distribution undergoes a sudden change of character. With $\lambda > 0$, $c'/c'' \to 0$, and the liquid is practically a nonsolvent; with $\lambda < 0$, $c'/c'' \to \infty$, and the liquid is a perfect solvent. This prediction accords with Brønsted and Volquartz's work on the solubility of high-molecular polystyrenes[66], which shows a very sharp separation of liquids into nonsolvents and perfect solvents. Schulz[67] extended this concept to mixed liquids, by assuming in this case that λ is a linear function of the liquid composition.

By considering a mixture of solvent and nonsolvent, the proportion γ of the latter in the critical mixture which is just a solvent was shown to be given by an equation of the form:

$$\gamma = A + B/M \tag{25}$$

where A and B are constants. This equation has been shown to represent satisfactorily the data for a number of synthetic polymers[68].

Notwithstanding the apparent success of these theories, it has been pointed out by Gee and Treloar[20] that their fundamental assumption is unsound. These authors showed experimentally that the molar entropy of solution of rubber in benzene is large compared with the heat of solution, and that it is proportional to the molecular weight of the rubber. Equations (24) and (25) therefore require another explanation; a possible one is suggested below.

The equilibrium distribution of rubber between two phases has also been examined by Flory[23], Huggins[24], and Gee[69]. The conditions for equilibrium between two phases $'$ and $''$ may be put in the form:

$$\left.\begin{aligned} \Delta G_0' &= \Delta G_0'' \\ \Delta G_r' &= \Delta G_r'' \end{aligned}\right\} \tag{26}$$

where the subscripts $_0$ and $_r$ refer respectively to liquid and to rubber[70]. The free energies are then expressed in terms of the heats and entropies of mixing. The latter is taken to be that given by the calculations described in the first section of this report, but a simple-power law is usually assumed for the heat. Thus, Flory writes, for each phase:

$$\begin{aligned} \Delta G_0 &= \Delta H_0 - T\Delta S_0 \\ &= kv_r^2 + RT\{\ln v_0 + v_r(1 - M_0/M)\} \\ \Delta G_r &= kMv_0^2/M_0 + RT\{\ln v_r - v_0(M/M_0 - 1)\} \end{aligned} \tag{27}$$

The assumption involved in writing down these equations is that the rubber may be treated simply as a liquid, a point of view which finds justification

both in its mechanical properties (which demonstrate the great freedom of the molecules to move relative to one another) and in the agreement with this theory found experimentally by Gee and Treloar. If Equation (27) is used to give the free energies in terms of composition, Equations (26) give two simultaneous equations from which v_r' and v_r'', the concentrations of rubber in the two phases, may be calculated. No simple algebraic solution is possible, but Flory has given a graphical solution for several values of k. His conclusion is that, for any value of k, there exists a critical temperature above which rubber is miscible with the liquid in all proportions. The composition of the critical mixture is given by:

$$(v_r)_{\text{crit.}} = 1/(\sqrt{M/M_0} + 1) \tag{28}$$

Since, for rubber, $M/M_0 \simeq 4 \times 10^4$, $(v_r)_{\text{crit.}} \simeq 0.015$. At a lower temperature, a two-phase system results, in which the dilute phase has a concentration $< (v_r)_{\text{crit.}}$. Indeed, except within a few degrees of the critical temperature, the dilute phase would be indistinguishable experimentally from pure solvent. The concentrated phase consists of a highly swollen gel, in which the calculated rubber content at a temperature 10° below the critical is only 10 per cent.

A similar analysis was carried through by Gee[69], using a more complex expression for the heat of mixing, *viz.*:

$$\Delta H_0 = \alpha(1 + \beta)M_0[v_r/(1 + \beta v_0)]^2 \tag{29}$$

The essential features of the solution are the same as in that of Flory, but it is possible to have a two-phase system in which the two phases are considerably more concentrated than is permitted by Flory's analysis.

It is of interest to try to find the relationship between this method of analysis and Brønsted's Equation (24), since the latter has in practice proved so useful. If this equation were strictly true, it should be derivable from the solution of Equations (26) and (27). Although this cannot be done rigorously, a similar equation may be derived by the following approximate method.

Combining the second equilibrium condition of Equation (26) with (27) we obtain:

$$\ln \frac{v_r'}{v_r''} = -\frac{kM}{M_0RT}\{(v_0')^2 - (v_0'')^2\} + (v_0' - v_0'')\left(\frac{M}{M_0} - 1\right) \tag{30}$$

The phase $'$ represents a dilute solution, for which we may write $v_0' \simeq 1$. The results of the complete analysis described above show that the composition of the second phase is almost independent of M. This is confirmed by experiment[67], so that v_0'' may be treated as a constant. Equation (30) thus takes the form:

$$\ln v_r'/v_r'' = M(a - b/RT) \tag{31}$$

where $a = (1 - v_0'')/M_0$; $b = k\{1 - (v_0'')^2\}/M_0$. The functions a and b are not strictly independent of T, and it is evident that Equation (31) differs formally from (24) only in predicting a more complex dependence on temperature. In fact, it is precisely in regard to temperature variation that Schulz's equation fails[67]. This analysis thus provides a reason for the formal success of the Brønsted-Schulz equations, while at the same time giving a different, and more satisfactory, interpretation of the constants.

The analysis described so far has considered the rubber as homogeneous, and we have now to enquire what modifications result when a mixture of rubbers

of different molecular weights is present. In the course of a fractionation by any equilibrium method (see below) we obtain two phases, each containing a portion of the rubber. The problem is to calculate the molecular-weight distribution in the two fractions, given that of the total rubber. Schulz examined this problem by assuming that the distribution of each molecular species $_i$ between the two phases was given by a modification of Equation (24), which may be written:

$$\ln c_i'/\alpha c_i'' = -\lambda M_i/RT \tag{32}$$

α was treated as an empirical constant, characteristic of the solvent and polymer and independent of M_i. By applying this equation to a range of M_i values, Schulz obtained graphically distribution curves for the fractions resulting from separating a rubber of given molecular distribution under various conditions. An important practical conclusion was that the efficiency of separation should be improved by keeping the concentration of the dilute phase as low as possible. There is no obvious justification for the arbitrary introduction of the constant α, and it should be further pointed out that this theory makes no attempt to examine the mutual effect of the different rubbers on their several solubilities. To solve the problem completely, we require to know the entropy of mixing ΔS^m of n_0 solvent molecules with n_i rubber molecules of molecular weight M_i, where $_i$ is to be given all values. Gee[69] suggested for this purpose an empirical extension of Flory's equation[23] to give the form:

$$\Delta S^m = -k\{n_0 \ln v_0 + \sum n_i \ln v_i\} \tag{33}$$

On this basis, it was shown that the distributions of two molecular species $_i$ and $_j$ between the two phases were related by the equation:

$$\frac{1}{M_i} \ln \frac{v_i'}{v_i''} = \frac{1}{M_j} \ln \frac{v_j'}{v_j''} \tag{34}$$

Extended to a wide distribution of rubbers, this analysis[71] confirms Schulz's findings[72] regarding the effect of concentration on the efficiency of fractionation, and indeed leads to the conclusion that a "fractionation" in which the concentration of the dilute phases exceeded 1 per cent would effect scarcely any separation at all, even of a complex mixture. The practical importance of such a conclusion requires no emphasis.

Before describing the experimental data, we may enquire how far the analysis would be expected to apply to rubber. The first criticism to be made is a general one. We have found, in the viscous behavior of rubber solutions, evidence that the entropy of solution is less in a bad solvent (ΔH_0 large) than in a good one. It is clear, therefore, that an approximation is involved in assuming the entropy of mixing, which is calculated for an ideal solvent, to apply to a liquid on the borderline between solvent and nonsolvent. Again, much of the work on solubility has been carried out with mixtures of solvent and nonsolvent. Hitherto, such a mixture has been treated simply as a simple liquid, whose properties are intermediate between those of its components. Actually, this is valid only to a first approximation, since in general the two liquids are differently distributed between two phases in equilibrium[66]. No systematic study of such a system has yet been published. A final point is that, throughout the analysis, we are concerned either with a homogeneous substance or with a homologous series of similar polymers. This is doubtless a very good approximation in the case of many synthetic polymers, but rubber, as normally

handled, is far from being adequately described in this way. The protein present in latex is most tenaciously retained by the solid rubber, and may profoundly modify its solubility behavior. In many cases, as we shall see, its effect may well be so large as to mask entirely the effect of molecular weight differences.

Rubber has long been known to be capable of separation, by treatment with solvent, into portions of very different solubility. It was formerly considered[73] that two sharply defined portions termed sol and gel were present, of which only the former was soluble. The usual method of separating these consists in extraction with light petroleum, or ethyl ether, but a careful study of the process[74] revealed that the boundary was ill defined, and that the sol portion was greatly diminished if care was taken to exclude oxygen. Kemp and Peters found that only 4–10 per cent of some of the rubber samples they examined was extracted by hexane after 3 days. Using other extractants[75], they obtained much larger amounts of sol, but even chloroform (the best liquid tried) extracted only 62 per cent of latex film after 3 days at 25°, without shaking. Actually, all samples of raw rubber examined by the present author could be completely dispersed in solvent if sufficient time was allowed, and agitation employed, although oxygen was rigorously excluded.

The failure of rubber to disperse easily and completely in hydrocarbon solvents is very surprising, and quite inexplicable if we regard rubber merely as a mixture of long straight-chain hydrocarbons. As we have noted above, cyclohexane should be a perfect solvent for rubber, but in fact even a purified rubber hydrocarbon disperses with some difficulty, giving "ropy" solutions at relatively low concentrations. Benzene is considerably superior in this respect, although the rubber is more easily precipitated from it by alcohol than from cyclohexane[76]. A still better solvent, from the point of view of obtaining clear mobile solutions, is a mixture of benzene with several per cent of an alcohol. Such a mixture disperses gel rubbers which are insoluble in benzene alone, while small additions of alcohol greatly increase the solvent power of hexane[75]. It appears probable that we are dealing here with two distinct factors. The lack of fluidity in the solvent which is best thermodynamically (*i.e.*, for which $\Delta H_0 = 0$) arises from the greater space occupied by the average molecule in such a solvent (cf. discussion on viscosity, above), which leads to structural viscosity. Addition of alcohol reduces this effect, and at the same time assists in separating the chains where they are held by the polar interactions between protein molecules.

It is quite unnecessary to assume, with Kemp and Peters, that sol rubber is necessarily an oxidation product of gel rubber. It is well known that oxidation promotes degradation of the rubber chains to more soluble products, but there is every reason to believe—from the thermodynamic study of Gee and Treloar[20]—that a linear, unoxidized rubber of any molecular weight whatever would be completely soluble in benzene. The fact that complete solution of rubber can be achieved experimentally also rules out the possibility of insolubility arising from chemical cross-links between the molecules. The final suggestion is that the protein remaining in association with the rubber is connected with the difficulty of dispersing it. Direct evidence that this is the true explanation is provided by the well-known fact[74] that the gel rubber contains practically the whole of the nitrogen. The nature of the association between rubber and protein is unknown, but its profound effect on the solubility of rubber is evident when we examine the various attempts which have been made to fractionate rubber.

Two general methods of fractionation have been adopted, based severally on the greater speed of solution of the shorter molecules, and on their greater solubility in critical mixtures of solvent and nonsolvent. In almost all cases the initial material used contained appreciable percentages of nitrogen, and there is abundant evidence that this is a complicating, if not actually the controlling factor. This is shown very clearly in the early work of Midgley, Henne and Renoll[77]. Using a carefully controlled fractional precipitation method, they obtained a series of products whose nitrogen contents increased as their solubility decreased. Although the initial material was completely soluble, they obtained finally an insoluble residue containing 4.21 per cent of nitrogen. Similar results were obtained in the very careful work of Bloomfield and Farmer[78]. By repeated extractions with acetone-light petroleum mixtures of increasing petroleum content, they concentrated the bulk of the nitrogen in a residue of greatly reduced solubility. Their earlier fractions were, however, substantially nitrogen free, and it was shown[79] that the molecular weights of these fractions were related to the composition of the extractant by an equation of the form (25). Kemp and Peters[80] employed the other method of separation, and obtained, by diffusion into hexane, a series of fractions of increasing molecular weight. Later[75] they were able to extract small quantities of very low molecular-weight material by using hexane-acetone mixtures as extractant. A further complication is revealed when the most soluble fracfractions of rubber are examined. Roberts[81] and Bloomfield and Farmer[78] obtained materials of molecular weight 30,000–60,000 which contained 1–3 per cent of oxygen. Roberts called his product caoutchol, and showed that it possessed some extremely interesting physical properties, which have not yet been fully explained.

It is evident that the solubility behavior of rubber is far more complex than would be explicable by the idealized picture of it which forms the basis of the theoretical treatment, and little progress has yet been made in the application of these ideas to rubber. This is due in part to the experimental difficulties arising both from the protein content and from the ready oxidizability of rubber, and in part to the use of much too high concentrations in most of the attempted fractionations of rubber. It must be concluded that nothing approaching a complete fractionation of rubber has yet been achieved, and the evidence that a considerable proportion of rubber is reasonably homogeneous[82] is almost certainly spurious.

Limited Swelling

Closely related to the problem of solubility is that of swelling. When a soluble, high-molecular rubber is covered with solvent, it rapidly imbibes the solvent, increasing in volume without (in the early stages) much change of form. After a time, dispersion slowly takes place and a solution is produced. The phenomenon affords a visual indication of the difficulty of dispersing long-chain substances: the rate of diffusion of solvent into the rubber greatly exceeds that of the rubber outwards. If the liquid employed is a nonsolvent, or the rubber is vulcanized, dissolution does not occur, but the rubber swells to a more or less well-defined equilibrium size. In measurements carried out in air, a definite limit is seldom observed, an initial rapid swelling being succeeded by a relatively slow absorption which continues indefinitely. The second stage, termed the increment by Scott[83], is absent when oxygen is carefully excluded[84], and should evidently be neglected in calculating the true equilibrium swelling.

The literature records an enormous number of swelling measurements, but their unsystematic nature renders many of them valueless from a scientific point of view. Whitby, Evans, and Pasternack[64] have provided data for a large range of liquids on the same rubber, and their work forms a useful basis on which to build or test any theory of swelling. These authors have drawn from their figures a number of interesting generalizations. Hydrocarbons in general are good swelling agents, the swelling being greatly diminished by the presence of a polar group, especially OH or CN. The effect of a given group is greatly diminished by a long hydrocarbon chain, and is less in aromatic compounds than in aliphatic. Addition of chlorine to the molecule usually enhances swelling.

A completely satisfactory theory of swelling should account quantitatively for these measurements; we are at present very far from such a state. The first attempt at a quantitative theory was made by Ostwald[85], who proposed a relationship between the swelling Q (cc. of liquid per cc. of rubber) and the dielectric constant ϵ of the liquid, *viz.*:

$$Q = K\epsilon^{-2.16} \tag{35}$$

Accumulation of more data soon revealed the inadequacy of this expression, and it was later suggested[86] that swelling was a function of μ^2/ϵ and the surface tension σ, μ being the dipole moment. These two quantities have been combined by Takei[87] into the single parameter $\mu^2/\sigma\epsilon$. There seems, however, little justification, either theoretical or experimental, for these suggestions.

The thermobyndamic criterion for equilibrium swelling is given, of course, by $\Delta G_0 = 0$, or $\Delta H_0 = T\Delta S_0$. For raw rubber we may express ΔS_0 in terms of composition by one of the theoretical equations, or may take the measured values for benzene. The entropy of swelling of vulcanized rubber has not been measured, but will clearly be lower than that of raw rubber, since cross-linking reduces the number of possible configurations of the molecule. This effect depends on the degree of vulcanization, and probably is important only at fairly high degrees of swelling. A semi-empirical method of deducing ΔS_0, for the vulcanizate used by Whitby and his coworkers, was suggested by Gee[38]. If we then write $\Delta H_0 \simeq k_0 v_r^2$, the equilibrium condition becomes:

$$T\Delta S_0/v_r^2 \simeq k_0 \tag{36}$$

where the left-hand side is assumed to be the same for all liquids (although dependent on the state of vulcanization of the rubber), and k_0 is a constant characteristic of the liquid. The function $T\Delta S_0/v_r^2$ becomes infinite at $v_r = 1$, and decreases continuously to zero at $v_r = p$, say, thereafter becoming negative. The swelling Q is, of course, $Q = (1 - v_r)/v_r$, and is therefore a function of k_0, which we can easily evaluate from Equation (36). The curve resulting from Gee's estimate of the entropy of swelling is shown in Figure 4. We have now to consider whether k_0 can be related to any other property of the liquid, and for this purpose we assume the relationship derived for simple liquids by Hildebrand[88] and Scatchard[89]. If E_0 and E_1 are the molar cohesive energies of the liquids, and V_0 and V_1 their molar volumes, we have:

$$k_0 = \alpha V_0\{\sqrt{E_0/V_0} - \sqrt{E_1/V_1}\}^2 \tag{37}$$

Applied to rubber, this requires us to know the cohesive energy density E_1/V_1 of rubber, and Gee has shown that a value of 66 cal. per cc. leads to values of

k_0 consistent with Whitby's swelling measurements. Equation (37) does not admit the possibility of negative values of k_0, and these are, indeed, to be ascribed always to specific interactions between the rubber and the liquid. Such cases being neglected, it is evident that $k_0 = 0$ when $E_0/V_0 = 66$, *i.e.*, rubber swells to its maximum extent in a solvent whose cohesive energy density is 66 cal. per cc. This is very close to the value (66.54) for cyclohexane[90]. Values of E_0/V_0 either higher or lower than 66 cal. per cc. give positive values

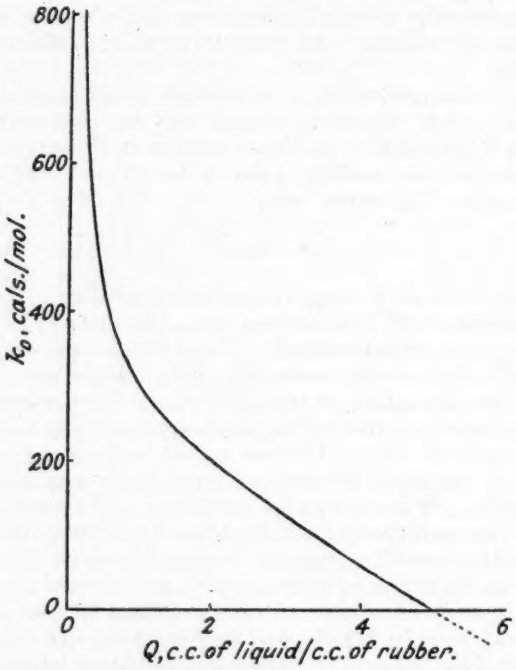

FIG. 4.—Relation between heat and extent of swelling of vulcanized rubber.

of k_0 and, therefore, lower values of Q. Hence, if we plot Q as a function of $x = \sqrt{V_0}\{\sqrt{E_0/V_0} - \sqrt{66}\}$, we should obtain a curve approximating in form to the error function, with its maximum at $x = 0$. Gee[36] has shown this to be roughly true, with certain well-defined exceptions. In the first place, aromatic and aliphatic liquids fall on separate curves, characterized by different values of α in Equation (37): this has not been satisfactorily explained. Highly associated liquids (alcohols, acids) give much too large Q values, showing the heat of swelling to be smaller than calculated. This is parallel to their behavior in admixture with low-molecular hydrocarbons[91]. Chlorinated liquids also give unduly high values of Q. This again is readily explicable by analogy with simple liquid systems, for their heats of mixing with hydrocarbons are generally small and frequently negative[92]. Although, then, the above theory is believed to give a sound basis for the understanding of swelling, it is clear that exceptions to the generalization will be frequent and may well be of great practical importance. Their elucidation, except in the above very crude way, has scarcely begun.

This review of the physical chemistry of rubber solutions reveals a field of work burdened with a mass of data which, until recently, were almost uncorrelated and imperfectly understood. Considerable theoretical advances have been made in the last few years, and they provide a sound foundation on which to build, but we still have a long way to go before anything approaching a complete understanding is achieved.

G. G.

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UNSATURATION OF POLYISOBUTYLENES AND BUTYL RUBBER

REACTIONS WITH NITROSOBENZENE, THIOCYANOGEN, IODINE MONOCHLORIDE, AND OZONE *

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Butyl rubber is an arbitrary name which is applied to rubberlike materials prepared by low-temperature copolymerization of isobutylene with diolefins[1]. As the properties of the polymer depend to a large extent on its unsaturation, it is important to be able to determine the concentration of diolefin units in the rubber. Experimental and analytical difficulties having thus far rendered it impractical to determine the unsaturation by analyzing the composition of the unreacted hydrocarbon mixture, a study was made of various reactions which can be carried out with the raw polymer.

As any reagent capable of reacting with a carbon-to-carbon double bond is potentially useful for determining unsaturation in Butyl rubber, several compounds were studied because of their general reactivity or previous use for similar purposes. In contrast to many olefins of low molecular weight, or even high polymers such as natural rubber, whose constitutions are well defined, the uncertainty in the unsaturation of Butyl rubber makes it evident that no single method of determining the double bonds in this material can be relied upon *a priori*. It was, therefore, considered desirable to determine unsaturation values by several independent methods, and to deduce in this manner results that might be considered as probably correct. With this viewpoint, the reactions of Butyl rubber with nitrosobenzene, thiocyanogen, iodine chloride, and ozone were studied, and the unsaturation values obtained by the use of these reagents were compared. Some parallel experiments were carried out with polyisobutylenes, since the very low degree of unsaturation of the latter materials serves as a good control for the Butyl reactions. In most cases isoprene copolymers of several different degrees of unsaturation were employed; however, some of the specific samples used in part of the earlier experiments were either unavailable in sufficient quantities or else the methods of synthesis were modified, and it was necessary in such cases to replace them in the later experiments with closely related, but not identical, polymers.

REACTION WITH NITROSOBENZENE

Bruni and Geiger[2] found that nitrosobenzene reacts almost quantitatively with natural rubber to form a nitrone. By employing the proper experimental conditions, Pummerer and Gündel[3] showed that this reaction could be used

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for determining rubber hydrocarbon:

$$\left[\begin{array}{l} \\ -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2- \end{array}\right] + 2C_6H_5NO \longrightarrow$$

$$\left[\begin{array}{l} \\ -CH=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{NO}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-CH_2- \end{array}\right] + C_6H_5NHOH \quad (1)$$

Since recent ozonolysis experiments[4] carried out with Butyl rubbers of various degrees of unsaturation have shown that practically all of the isoprene residues are present in the polymer chain as 1,4 addition units, nitrosobenzene would be expected to react with Butyl rubber in accordance with Equation 1. Experiments were carried out as follows: A freshly prepared benzene solution of nitrosobenzene was added to a solution of the rubber in the same solvent at room temperature, the air remaining in the flask was swept out with dry nitrogen, and the contents was allowed to stand in the dark for a certain time. The reaction mixture was then stirred into five volumes of acetone, the coagulum further purified by reprecipitation, the product vacuum-dried at 60–70° C, and analyzed for nitrogen by a modified semimicro-Kjeldahl procedure, in which

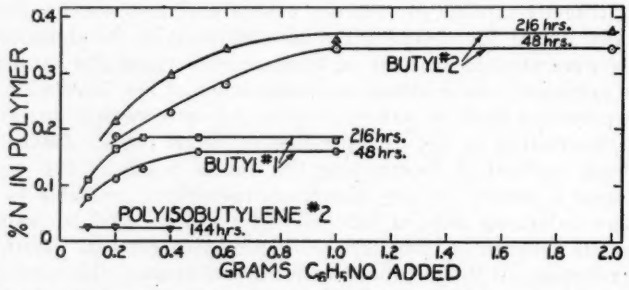


FIG. 1.—Effect of increasing proportions of nitrosobenzene on combined nitrogen (4 grams polymer in 100 cc. of benzene, reagent dissolved in 10 cc. of benzene).

phosphorus and hydriodic acid were used as the reducing medium. The probable error in the nitrogen analyses was about 1 per cent (based on the nitrogen) for the Butyl rubber reaction products, and 2–3 per cent for the polyisobutylene products. The raw polymers used for these experiments were stored in solid carbon dioxide when not in use, and were vacuum-dried at 60–70° before making up the solutions. The benzene used was C.P. grade, and was not further purified. The nitrosobenzene was obtained from the Eastman Kodak Company (melting point, 64–66° C). On a few occasions this reagent was not used immediately, and it was then found to have decomposed partially with discoloration. Purification by steam distillation yielded a colorless product, which appeared to be satisfactory for these experiments.

When the reaction was allowed to proceed at steam-bath temperatures without exclusion of air, it occurred much more rapidly, but the resulting products were very sticky and of low molecular weights, as indicated by viscosity measurements, an indication of rather severe oxidative degradation.

Similar observations were made by Pummerer and Gündel[3] for natural rubber. In these instances a large proportion of the Butyl reaction product was lost through emulsification when coagulation with acetone was attempted. Most, but not all, of the degradation could be eliminated by carrying out the reaction under nitrogen at room temperature; but usually some emulsification took place, even under these conditions, when the reaction had been allowed to proceed for several days or longer.

Figure 1 shows the effect of reagent concentration on combined nitrogen at several reaction times. As might be expected, the amount of reagent required to obtain a plateau value is greatest for the polymer having the highest unsaturation. In view of evidence presented below, it is unlikely that the polyisobutylene contains as much unsaturation as is indicated by the curve in Figure 1 for this polymer; the latter value is therefore regarded as a blank representing, primarily decomposition effects of the reagent when dissolved in benzene[5].

The effect of the time of reaction on combined nitrogen is shown in Figure 2.

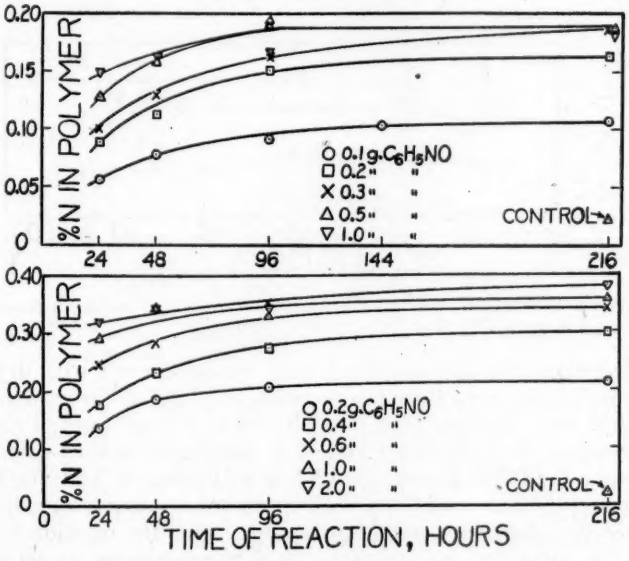


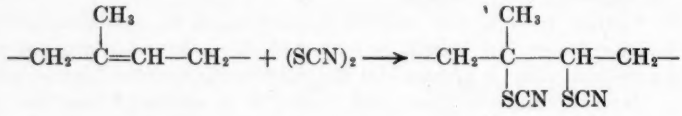
FIG. 2.—Rate of reaction of nitrosobenzene with butyl samples 1 and 2 (4 grams polymer in 100 cc. of benzene; reagent dissolved in 10 cc. of benzene).

Inconveniently long intervals (over 100 hours) are required to reach constant values. From the data obtained after 216 hours, corrected for the polyisobutylene blank, unsaturation values of 0.64 and 1.38 are found for Butyl samples 1 and 2, respectively. These values are expressed as the percentage ratio of moles of isoprene units to moles of isobutylene units ("mole per cent") in the polymer.

REACTION WITH THIOCYANOGEN

Kaufmann and Gärtner[6] showed that thiocyanogen may be used to determine ethylenic bonds. In applying this reagent to natural rubber, Pummerer and Stärk[7] found no advantages over the iodine chloride method; they found rather the disadvantage that only a short time interval exists during which

the reagent is constantly consumed, followed by a gradual decomposition of the excess reagent, presumably induced by either the rubber thiocyanide or by traces of liberated thiocyanic acid. Under suitable conditions they were, nevertheless, able to react thiocyanogen nearly stoichiometrically with the rubber hydrocarbon and thus to determine the amount of unsaturation, in accordance with the reaction:



(2)

Tenth-molar solutions of thiocyanogen in anhydrous carbon tetrachloride that had been prepared by further purification[8] of the C.P. solvent were freshly made by Söderbäck's method[9], and were immediately added to solutions of Butyl rubber (in the same solvent) that had been previously cooled in ice

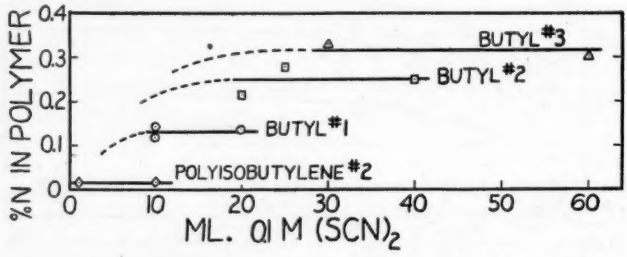


FIG. 3.—Effect of increasing proportions of thiocyanogen on combined nitrogen (3.33 grams polymer in 50 cc. of carbon tetrachloride, 72-hour reaction).

water. The air above the mixed solutions was swept out with dry nitrogen, and the sealed flasks were stored in the dark at 10–12° C for various intervals. The reaction products were then precipitated in five volumes of C.P. acetone, and the coagula were squeezed into thin films and Soxhlet-extracted with warm acetone for 15–24 hours. According to Pummerer and Stärk[7], acetone extraction under these conditions is adequate for removing any thiocyanogen polymer $(SCN)_x$ that may have been formed during the reaction with natural rubber. The extracted coagula were then vacuum-dried at 60–65° C, and analyzed for nitrogen and sulfur. The former was determined by the modified Kjeldahl method mentioned above, and the sulfur was determined by the Parr bomb method or, in some cases, by combustion in a Braun-Shell sulfur apparatus. The analysis of both of these elements served as a check on the accuracy of the analytical procedure and on the possible occurrence of side reactions (other than polymerization of the reagent), since the molar ratio of nitrogen to sulfur in the products should be unity for simple addition. The reproducibility of the nitrogen analyses was about 1 per cent for the Butyl derivatives and 2–3 per cent for those of polyisobutylenes. That of the sulfur analyses was about 2–3 per cent for the Butyl rubber samples, but sometimes no better than 5–10 per cent for polyisobutylenes. In the samples containing relatively low percentages of sulfur, greater significance is therefore attached to the nitrogen analyses. By careful control of the reagents and the procedure, it was possible to attain a precision of 10 per cent or less in independent trials.

Figure 3 shows the effect of reagent concentration on the value of combined nitrogen after a fixed reaction time (72 hours) for several polymers of varying degrees of unsaturation. It is observed that the amount of reagent may be varied over a considerable range without altering the analytical values. Figure 4 shows the effect of varying the reaction time. The inordinate rise in the

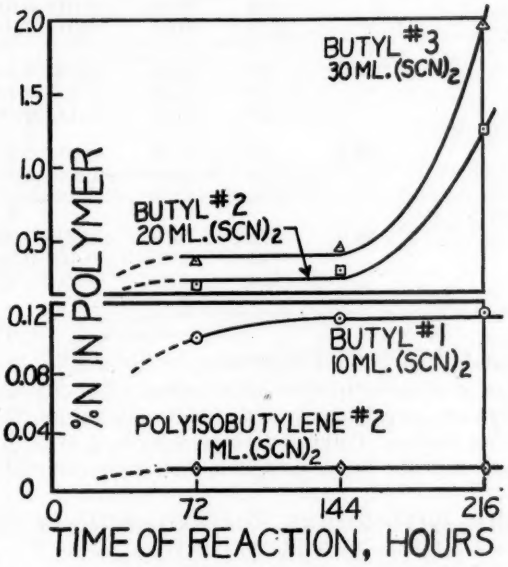


FIG. 4.—Rates of reaction of thiocyanogen with polyisobutylene and with Butyl rubbers (3.33 grams polymer in 50 cc. of carbon tetrachloride, 0.1 *N* reagent).

sulfur and nitrogen contents of Butyl 2 and Butyl 3 after long periods of reaction suggests the possible presence of $(SCN)_x$ in these products. To obtain information on this point, 0.1 *M* solutions of thiocyanogen in carbon tetrachloride were allowed to stand for 216 hours at 10–12° in both daylight and darkness. The $(SCN)_x$ that had been formed in this interval was filtered off and washed with acetone; its amount and solubility in acetone were determined with the following results:

	Percentage of original $(SCN)_2$	Solubility in boiling acetone, (g. per 100 cc.)
Dark reaction	2–3	0.0025
Daylight reaction	20	0.046

These results indicate that thiocyanogen polymer formed under these experimental conditions would be difficult to remove from the reaction product by the method of extraction employed by Pummerer and Stärk[7], although the latter workers did not require such long reaction periods, and doubtless obtained a more soluble $(SCN)_x$ than was the case in these experiments. The results therefore indicate that, to introduce the minimum error, the Butyl reactions must be carried out in the dark, below room temperature, with the minimum amount of reagent necessary for addition within a reasonable time interval.

TABLE I

COMPOSITIONS OF THIOCYANOGEN DERIVATIVES

Polymer[a]	0.1 *M* $(SCN)_2$ (cc.)	Reaction time (hrs.)	Sulfur (%)	Nitrogen (%)	Moles sulfur / Moles nitrogen
Polyisobutylene sample 1	1.0	72	0.03	0.016–0.016	0.82
		144	0.03	0.016–0.016	0.82
		216	0.02	0.014–0.014	0.62
Butyl sample 1	10.0	72	0.28	0.134–0.133	0.92
		144	0.28	0.131–0.129	0.94
		216	0.27	0.144–0.143	0.82 (?)
Butyl sample 2	20.0	72	0.46	0.214–0.217	0.93
		144	0.69	0.310–0.304	0.98
		216	2.71	1.28 –1.28	0.93
Butyl sample 3	30.0	72	0.76	0.328–0.330	1.01
		144	1.07	0.498–0.501	0.94
		216	4.22	1.94 –1.95	0.95

[a] 3.33 grams dissolved in 50 cc. of purified carbon tetrachloride.

The analytical data in Table I show that, within the limits of experimental error, the molar ratio of sulfur to nitrogen is unity. The chemical unsaturation values of the polymers, as calculated from the horizontal portions of the curves in Figure 5, are as follows: Polyisobutylene sample 2, 0.03; Butyl sample 1, 0.24; Butyl sample 2, 0.48; Butyl sample 3, 0.80 mole-per cent.

REACTION WITH IODINE MONOCHLORIDE IN CARBON TETRACHLORIDE

The most common method for determining unsaturation in olefinic compounds is by the use of halogens or halogen derivatives. Of the considerable number of such reagents that have been employed for natural rubber, the most satisfactory from the standpoint of analytical expediency, as well as accuracy, has been iodine monochloride dissolved in glacial acetic acid (Wijs reagent). With natural rubber, and also with other materials of known structure, it is usually possible to adjust the experimental conditions in such a way as to obtain accurate and reliable values, although it has been recognized that "the addition of iodine monohalides is not satisfactory, however, as a *general* analytical method for ethylenic compounds"[10], principally because of the disturbing effects of substitution reactions, negative groups, and splitting off of halogens in operations subsequent to the principal reaction[11]. Böeseken and Gelber[12] preferred to use Marshall reagent (iodine monochloride dissolved in carbon tetrachloride), since they found that the nonpolar solvent gave less disturbing side reactions. With natural rubber Kemp[13] showed that quantitative results could be obtained rapidly, and with a minimum of substitution, by using Wijs reagent at 0° C. Pummerer and Mann[14] used chloroform as the solvent and, after applying a correction for substitution, found that excellent results could be obtained; however, the reaction was much slower than Kemp's, requiring several days for completion. Later, Pummerer and Stärk[7] changed to carbon tetrachloride, since this solvent bestowed greater stability on the reagent and minimized substitution. They obtained good results even at room temperature, provided not over 20 per cent excess reagent was used. Pummerer and Stärk acknowledged that the Kemp-Wijs method is advantageous

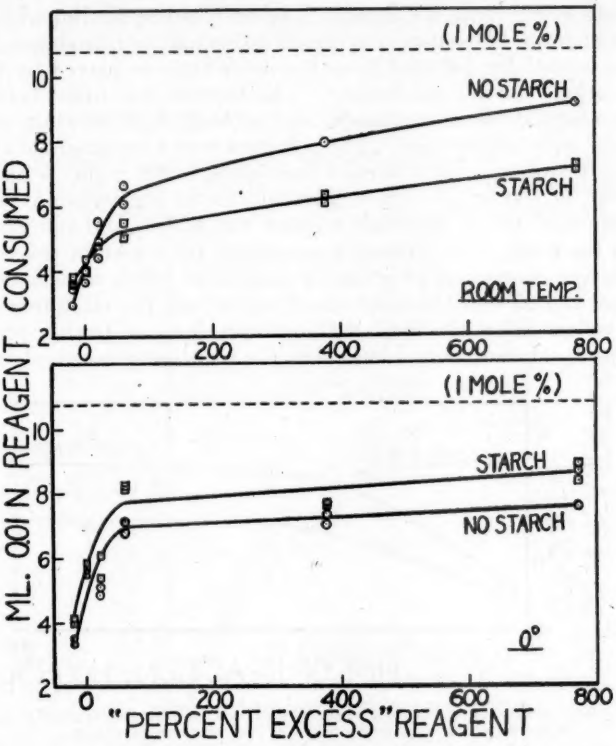


FIG. 5.—Effect of increasing proportions of Marshall reagent on amount of reagent consumed by Butyl sample 1 at room temperature and at 0° C (0.300 gram of polymer in 100 cc. of carbon tetrachloride, 5.75-hour reaction).

at 0° C, since a large excess of the reagent can then be added without substitution taking place.

Results of the halogen-halide reactions are usually unpredictable. For example[7], 3-methyl-2-butene behaves like rubber, either by Kemp's or by Pummerer and Stärk's method. On the other hand, 3-ethyl-2-pentene cannot be titrated by either method without the occurrence of an appreciable amount of substitution, and in this respect it resembles terpenes. Gorgas[15] claimed good results for raw rubber from a 15-minute reaction with iodine monobromide in carbon tetrachloride. On the contrary, Kemp and Mueller[16] obtained low values with the standard Gorgas method. Higher values were obtained when the reaction time was doubled, but the results were variable. These brief references are sufficient to show that, even with systems in which the difficulty of estimating small amounts of unsaturation does not arise, chemical complications of an unforeseen nature may readily obstruct the direct application of the halogen-halid reactions.

In studying the behavior of Marshall reagent with Butyl rubbers, it was considered advantageous to use more dilute reagent solutions, since the resulting titer is invariably small. Purified carbon tetrachloride[8] was used as the solvent, both for the polymers and for the reagent, which was Eimer and Amend's C.P. grade, further purified by one recrystallization of the melt. All

reactions were carried out in the dark. Aside from the dilution of the reagent and of the sodium thiosulfate, no modifications were introduced that were regarded as essentially different from the procedures employed by Kemp and by other workers for natural rubber. The solvent was dried before use by distillation over potassium carbonate, and a blank determination was carried out in parallel with each sample. The polymers were vacuum-dried at 60–70° C before being dissolved. As a typical procedure, 0.300 gram of Butyl rubber was dissolved in 100 cc. of carbon tetrachloride in a glass-stoppered flask, a certain volume of 0.01 *N* Marshall reagent was added, and the flask allowed to stand in the dark at the desired temperature for a certain time. Then 10 cc. of a solution containing 15 grams of potassium iodide in a mixture of 100 cc. of alcohol and 25 cc. of distilled water was added, the mixture was titrated to a light yellow color with 0.01 *N* thiosulfate, 5 cc. of freshly prepared 0.2 per cent starch solution were added, and the titration was completed. Since

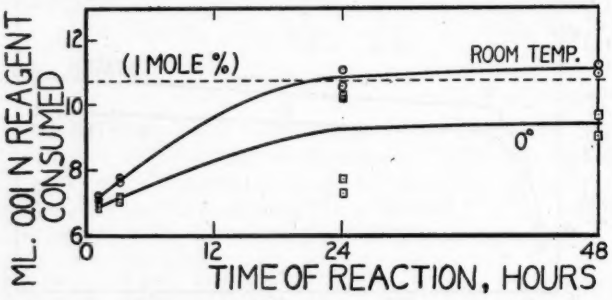


FIG. 6.—Rate of reaction of Marshall reagent with Butyl sample 1 (0.300 gram of polymer in 100 cc. of carbon tetrachloride, 200 "per cent excess" reagent).

carbon tetrachloride is a very sensitive internal indicator for free iodine, it was possible in this series of experiments to determine whether the use of starch introduced an appreciable error. In experiments at 0° C, the polymer solutions were cooled to this temperature, before addition of reagent, by immersion in ice water, and the flasks were allowed to stand in the cooling mixture in the dark for the chosen intervals.

Figure 5 shows the effect of adding various amounts of iodine monochloride on the amount of reagent consumed in 5.75 hours at room temperature. The "per cent excess" reagent is arbitrarily expressed on the assumption of 1 mole-percentage of unsaturation in the polymer. The individual points represent independent experiments, which were usually found to check within about 5 per cent. The precision of duplicate analyses was about the same order. The apparent difference between the two curves, indicating the influence of the starch indicator, is almost within the overall experimental error; this, in conjunction with the reversed position of the two curves in the 0° C experiments (Figure 5), shows that the use or omission of the indicator does not have any consistent effect on the results. Comparison of the curves obtained at the two temperatures reveals a smaller but still positive slope for reagent consumption at 0°, which may be interpreted as the result of suppressing substitution. Figure 6 shows the influence of the time of reaction for a fixed amount of added reagent (200 "per cent excess"). Somewhat higher values are again observed at room temperature, and constant values are not realized for reaction periods

of less than about 24 hours. If the 0° C value is accepted as the more significant, an unsaturation value of about 0.88 mole-per cent is obtained for Butyl sample 1.

REACTION WITH IODINE MONOCHLORIDE IN ACETIC ACID

A series of experiments similar to those described in the preceding section was carried out with 0.01 *N* Wijs reagent; C.P. carbon tetrachloride rather than the repurified substance was used as the polymer solvent. Figure 7

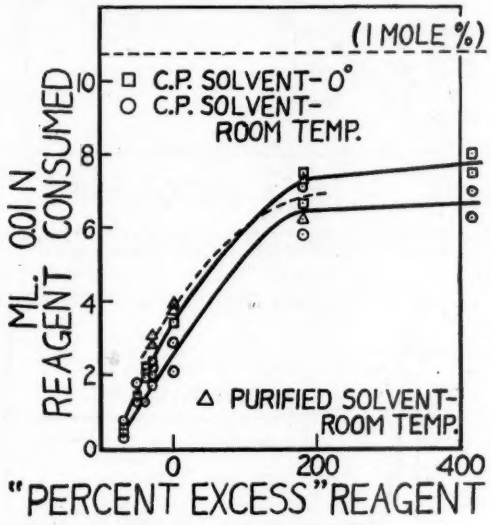


FIG. 7.—Effect of increasing amounts of Wijs reagent on amount of reagent consumed by Butyl sample 1 (0.300 gram polymer in 100 cc. of carbon tetrachloride, 5.75-hour reaction).

shows that this replacement has no significant effect. Starch was used as the indicator. For a reaction period of 5.75 hours it is observed that, when amount of reagent consumed is plotted as a function of amount added, roughly constant consumption takes place beyond about 200 "per cent excess" of reagent; furthermore, no significant difference is found between the results obtained at 0° C and at room temperature.

When the amount of reagent is fixed at 200 "per cent excess" and the reaction time is varied, the effects of increased substitution at the higher temperature become more marked. Figure 8 shows that reagent consumption becomes constant after about 24 hours at 0° C, but continues to rise for at least 72 hours when the reaction proceeds at room temperature. From the curve obtained at the lower temperature, the unsaturation of Butyl sample 1 is found to be 1.0 mole-per cent. If the concentrations of the reagents are increased to 0.1 *N* and about 500 "per cent excess" of reagent is used at room temperature for a reaction period of 1 hour (conditions more directly comparable to the Kemp-Wijs method), unsaturation values of 0.8–1.0 mole-per cent are obtained for Butyl sample 1. Apparently the effects of using a great excess of reagent and of increased substitution at the higher temperature are compensated by the shorter reaction period[17].

REACTION WITH OZONE

Of ozonized air containing about 0.25 volume-per cent of ozone is passed through a solution containing 10–15 grams of Butyl rubber dissolved in 100–200 cc. of purified carbon tetrachloride at 0° C, the viscosity of the solution rapidly decreases. Removing samples from time to time, recovering the polymer by evaporation, and determining its intrinsic viscosity at 20° C in diisobutylene[18]

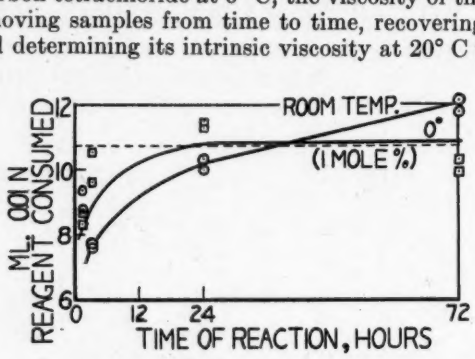


FIG. 8.—Rate of reaction of Wijs reagent with Butyl sample 1 (0.300 gram polymer in 100 ml. carbon tetrachloride, 200 "per cent excess" reagent).

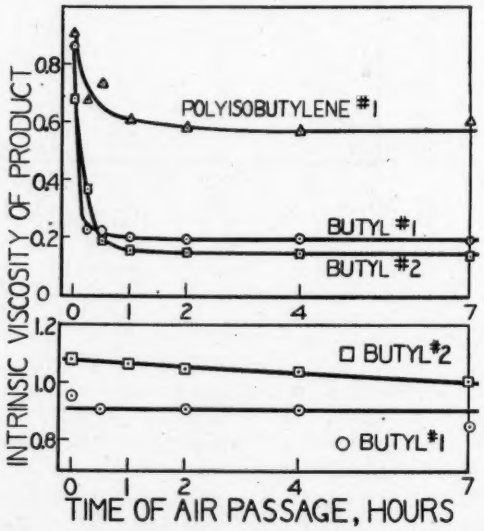


FIG. 9.—Rate of degradation of polyisobutylene and Butyl rubbers by ozone and by air.

gives curves like those in Figure 9. These show that the intrinsic viscosity of the polymer reaches a minimum within 2 hours under the conditions described above, the viscosity then remaining constant for at least an additional 5 hours. If the ozone concentration is reduced two-fold or three-fold, the same characteristic value is obtained, within the limits of experimental error, for the minimum viscosity; the only difference now is that a proportionately longer time is required to attain the minimum.

It is reasonable to suppose that the polymer chain is cleaved at the double bonds by the action of the ozone or by air catalyzed by ozone; the limiting

viscosity is thus a measure of the mean size of the polymer fragments existing originally between successive double bonds. Figure 9 shows that the passage of air alone through the solution under the conditions of these experiments has no appreciable effect on the resulting intrinsic viscosities.

If the above view is correct, the limiting viscosity makes it readily possible to determine the amount of unsaturation present in the original polymer. To arrive at this value it is first necessary to convert the viscosity-average molecular weight corresponding to the measured limiting viscosity to the number-average. If the degradation occurs in a random manner it can be shown that the conversion factor is 1.832. According to Flory[18] the viscosity-average molecular weight $\bar{M}_v$ for polyisobutylene dissolved in diisobutylene is given by:

$$\bar{M}_v = [\sum_i N_i M_i^{a+1} / \sum_i N_i M_i]^{1/a} \tag{3}$$

where $a = 0.64$, and N_i and M_i are the number and molecular weight of species i. For random cleavage:

$$N_i = N(1 - p)p^{i-1} \tag{4}$$

where p is the probability of cleavage. Substituting (4) into (3), and changing the summation in the numerator to an integral, we obtain, since $M_i = iM_o$, where M_o is the molecular weight of the monomeric unit:

$$\bar{M}_v = \left[\int_0^\infty N(1 - p)p^{i-1}(iM_o)^{a+1} di / \sum_i N(1 - p)p^{i-1} iM_o \right]^{1/a} \tag{5}$$

Since

$$\sum_i N(1 - p)p^{i-1} iM_o = M_o N/(1 - p) \tag{6}$$

we obtain:

$$\bar{M}_v = \left[(M/p)(1 - p)^2 \int_0^\infty i^{a+1} p^i di \right]^{1/a}$$

$$\cong [(1 + a)\Gamma(1 + a)]^{1/a}/(1 - p) \tag{7}$$

Since the number-average molecular weight is given by

$$\bar{M}_n = 1/(1 - p) \tag{8}$$

we find:

$$\bar{M}_v/\bar{M}_n = [(1 + a)\Gamma(1 + a)]^{1/a} = 1.832 \tag{9}$$

To learn whether complete cleavage at the double bonds occurs during ozonization, an experiment was carried out in which aliquot portions of the samples removed were further treated by refluxing with distilled water for about one hour to hydrolyze any ozonides that might have remained intact. The refluxed samples were then evaporated to dryness in a vacuum at 60–70° C, and their intrinsic viscosities compared with the corresponding untreated samples. Figure 10 shows that both procedures lead to the same viscosity curve. This fact indicates that complete cleavage of the double bonds occurs during ozonization.

Since the fragment molecules are of sufficiently low molecular weight, it is possible to obtain an independent confirmation of the unsaturation values deduced from the viscosity curve by chemical analysis of the end groups. Since substantially all of the isoprene residues are present as 1,4 addition units[4],

oxidative cleavage at the double bond should give rise to one carbonyl and one carboxyl (or aldehyde) group per double bond:

$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-\right] \xrightarrow{O_3} -CH_2-\overset{CH_3}{\overset{|}{C}}=O + HOOC-CH_2- \qquad (10)$$

End group determinations were carried out in the following manner: The solution of polymer in purified carbon tetrachloride was ozonized for 3 hours at 0° C, and the resulting solution was mechanically shaken with an excess of distilled water. The polymer was recovered by separation and evaporation, and aliquot samples were analyzed as described below. Since it was regarded as possible for the oxidative step to give rise to some aldehyde rather than

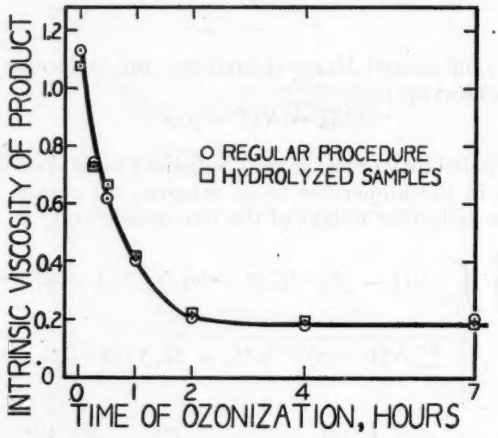


FIG. 10.—Effect of hydrolysis on intrinsic viscosity of degradation products from Butyl sample 1.

carboxyl groups, a further portion of the ozonized polymer solution was agitated with an equal volume of 5 per cent hydrogen peroxide for 3 hours, and the polymer was recovered and analyzed in the way just described. Weighed portions of the polymers obtained by these procedures were dissolved in carbon tetrachloride and in *n*-heptane, and were titrated with 0.05 *N* alcoholic potassium hydroxide to a phenolphthalein end-point. Other portions were converted to hydrazones by dissolving them in chloroform, heating the solutions for 1 to 3 hours with a suitable amount of 10 per cent solution of 2,4-dinitrophenylhydrazine freshly dissolved in glacial acetic acid, filtering when cool, and evaporating to dryness on the steam bath. The resulting coagula were then dissolved in petroleum ether (in which the excess reagent is insoluble), evaporated to dryness, dried in a vacuum at 65° C, and analyzed for nitrogen by the semimicro-Kjeldahl method; the unsaturation values were computed from the nitrogen content. Table II contains comparative data obtained by the viscosity and end group methods.

A number of runs not included in Table II showed that the viscosity unsaturation values were reproducible within 10 per cent. The end-group determinations were found to have about the same order of precision. It appears from the data in Table II that the carboxyl titrations in carbon tetrachloride give somewhat higher values than the corresponding ones in *n*-heptane, although the difference is barely outside of the probable error, and may not be

TABLE II

UNSATURATION (IN MOLE-PERCENTAGE) OF POLYISOBUTYLENES AND BUTYL RUBBERS ACCORDING TO VISCOSITY AND END GROUP DETERMINATIONS

Polymer	From viscosity	From KOH titration: Ozonized soln. treated with water	From KOH titration: Ozonized soln. treated with H_2O_2	From hydrazone analysis: Ozonized soln. treated with water	From hydrazone analysis: Ozonized soln. treated with H_2O_2
Polyisobutylene 1[a]	0.05	...	...	...	...
Polyisobutylene 1[b]	0.09	...	...	...	...
Polyisobutylene 2[c]	0.02	...	...	...	...
Butyl 1[d]	0.51	0.59; 0.62[e] 0.53; 0.55[f]	0.63; 0.64[e] 0.52; 0.58[f]	0.67; 0.69[g]	0.52; 0.53
Butyl 1[d]	0.57	0.46	0.48	...	...
Butyl 2[d]	0.86	0.96; 1.01[e] 0.78; 0.78[f]	1.05; 1.07[e] 0.90; 1.02[f]	0.95; 0.96[g]	0.88; 0.94
Butyl 2[d]	0.80	0.69	0.78	...	...

[a] A sample of intrinsic viscosity 1.3, fractionated to remove species having viscosity-average molecular weights less than about 50,000[18].
[b] A sample of the same class as 1, but from a later synthesis, and different feed stocks, fractionated in the same manner as 1.
[c] A sample of intrinsic viscosity 1.6 fractionated in the same manner as 1.
[d] Samples from different sheets.
[e] Titrated in carbon tetrachloride.
[f] Titrated in *n*-heptane.
[g] Probably high because of occluded reagent.

significant. Furthermore, the data indicate that in the course of ozonization no appreciable number of aldehyde end-groups are formed, since the treatment of the ozonized polymers with hydrogen peroxide does not lead to significantly higher unsaturation values.

SUMMARY OF RESULTS

Table III summarizes unsaturation values obtained for the various polymers. The ranges indicated are, in most cases, extreme values of determinations made with two or more different samples of a given polymer type. Taking into consideration the small amounts of unsaturation involved, the values based on end-group determinations are in reasonably good agreement with one another and with the values based on the viscosity of the degraded polymer. Higher values are observed for the nitrosobenzene determinations, but these are considered to be less reliable because of the ease with which oxidation phenomena can occur with this reagent. The thiocyanogen values are the lowest of all; on the basis of values obtained by the other methods as well as

TABLE III

UNSATURATION RANGE (IN MOLE-PERCENTAGE) OF POLYISOBUTYLENE AND BUTYL POLYMERS

Reagent	Polyisobutylene (Fractionated): Sample 1	Polyisobutylene (Fractionated): Sample 2	Butyl rubber: Sample 1	Butyl rubber: Sample 2
Nitrosobenzene	...	0 –0.08	0.64	1.4
Thiocyanogen	...	0.03	0.24	0.48
Iodine monochloride				
Marshall reagent	...	...	0.88	...
Wijs reagent	...	...	1.0	...
Concentrated Wijs reagent	...	0.04–0.4	0.8 –1.1	1.7 –2.0
Ozone-viscosity	0.05–0.09	0.02	0.51–0.57	0.80–0.86
Ozone–carboxyl titration	...	...	0.46–0.64	0.78–1.1
Ozone–hydrazone	...	...	0.52–0.69	0.88–0.96

of experimental evidence not included in this paper, these values are believed to result from incomplete reaction. As a class the iodine monochloride methods give considerably higher values than those obtained with the other reagents. This may be attributed to the substitution reaction that readily occurs with that reagent. The effect is perhaps most marked in the data obtained for polyisobutylene sample 2 with 0.1 *N* Wijs reagent; the upper value (0.4) is far greater than can be explained on the basis of the known molecular weight of this polymer[18] and the corresponding terminal double bond contribution. Furthermore, since this polymer sample was fractionated in such a way as to remove all species of viscosity-average molecular weight less than about 50,000, the high value cannot be ascribed to the presence of dimers, trimers, or other small molecules formed during polymerization.

In view of the data and the above considerations, it is believed that the unsaturation values based on ozone degradation are correct within the limits of experimental error, and that this reagent makes possible a relatively good estimation of the number of double bonds in polymers such as have been described. A modified procedure more suitable for rapid evaluations is the object of a current investigation.

ACKNOWLEDGMENT

The writer is indebted to Joseph Holowchak for developing the semimicro-Kjeldahl procedure used in many of the analyses, to (Mrs.) M. Robbins for securing much of the experimental data, and to P. J. Flory for coöperation in deriving the molecular weight relations.

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[16] Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
[17] Subsequent to completion of this manuscript, Kemp and Peters (*Ind. Eng. Chem. Anal. Ed.* **15**, 453 (1943)) published iodine values of several samples of Butyl rubber and a polyisobutylene. They used a modified procedure, in which a *p*-dicholrobenzene-chloroform mixture was employed as the rubber solvent. The values were similar to those obtained in this Laboratory for samples believed to be related closely to those studied in their work, and are in agreement with the conclusion of the present writer that substitution occurs readily with iodine monochloride. In regard to the results of Kemp and Peters, unsaturation values as large as 0.36 per cent for polyisobutylene have seldom been found in this Laboratory; although an upper limit of 0.4 per cent is listed in Table III for the Wijs reagent, the majority of our values for samples of polyisobutylenes that were fractionated to eliminate low ends are of the order of several hundredths of one per cent. For reasons made clearer in the body of this paper, and especially elsewhere (Flory, *J. Am. Chem. Soc.* **65**, 372 (1943)), the present writer cannot agree with the suggestion of Kemp and Peters that their value of 0.36 per cent be considered as a correction factor for results with Butyl rubber. It is likely, as they have indicated, that their sample of polyisobutylene contained a small percentage of very low isobutylene polymers, and that the latter accounted for their unsaturation value. However, the proportions of such components would doubtless vary from one sample to another, and would thus give a "correction term" that is not only constant, but does not genuinely represent the effect of the high-polymer end groups. It is much more likely that their (and our) iodine values for Butyl rubbers are too high because of factors inherent in the iodine monochloride reactions rather than because of the effect of polymer end-groups, the latter contribution being much less, in the light of our knowledge of the molecular weights of these polymers, than Kemp and Peters consider possible.
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SOLUBILITY AND DIFFUSION OF SULFUR IN SYNTHETIC ELASTOMERS *

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In a previous investigation[1] the solubility and rate of diffusion of sulfur in natural rubber were determined. The importance of these properties in connection with the vulcanization process was also discussed. The present paper presents data on the solubility and rate of diffusion of sulfur in various synthetic elastomers which are being used to replace natural rubber. A knowledge of sulfur solubility and diffusion will be an aid to a more intelligent approach to compounding problems arising from the broader use of the synthetics.

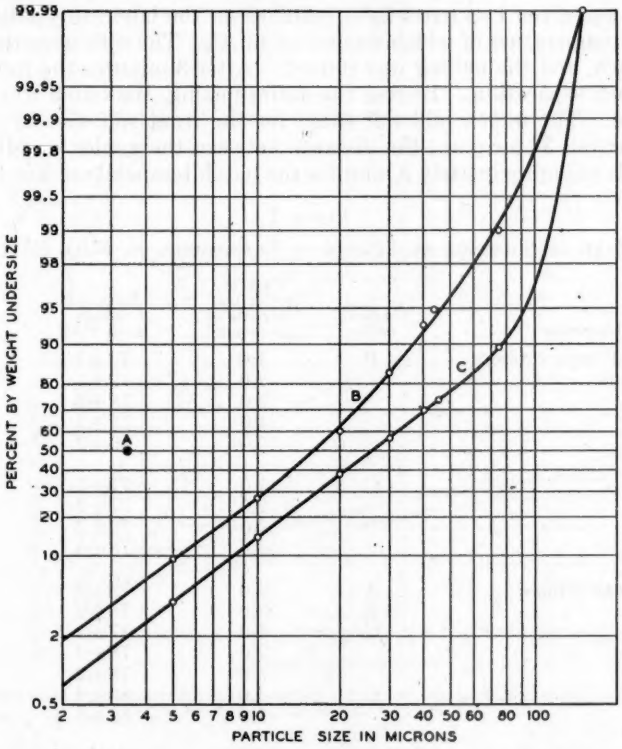

FIG. 1.—Particle size distribution of sulfur.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 36, No. 2, pages 109–113, February 1944. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in New York, October 5–7, 1943.

The elastomers studied were 75 butadiene–25 styrene copolymer (Buna-S or GR-S), butadiene-nitrile copolymer (Hycar OR-15), 75 butadiene-25 acrylonitrile copolymer (Stanco Perbunan), isobutylene-isoprene copolymer (Butyl B-3), polychloroprene (Neoprene-GN or GR-M), and natural rubber (Rubber Culture Maatschappij Amsterdam crepe).

Three grades of sulfur of different particle size and distribution were employed, and are designated A, B, and C. B and C are commercial grades of ground sulfur used in the rubber industry, and A is a micronized sulfur with an average particle size of 3 to 4 microns, according to the supplier. The particle size-distribution curves of the B and C samples are given in Figure 1.

RATE OF SOLUTION ON THE MILL

A study was made of the rate of solution of these sulfurs in various types of synthetic rubberlike polymers. To standardize the milling procedure, the following conditions were adhered to: A standard batch weight of 300 grams of elastomer was given two hand-tight refinings on the laboratory mill rolls, the initial roll temperature of which was set at 43° C. The rolls were then opened to 0.015 inch, and the milling was started. After 3 minutes the rolls were set at 0.045-inch separation. During the entire mixing, the batch was cut twice per minute. The 6-inch mill roll speed for the front roll was 25 r.p.m. and for the rear roll 35.5 r.p.m.; the distance between the guides was 10.2 inches. In intervals of approximately 5 minutes the batch temperature was taken with

TABLE I

RATE OF SOLUTION OF SULFUR IN ELASTOMERS ON MILL ROLLS

Elastomer	Grade of sulfur	Parts of sulfur per 100 parts of elastomer	Range of milling temp. (° C)	Time for solution (min.)
Natural crepe rubber[a]	B	1.0	72±1	4
		2.0	72±1	6
		3.0	78±2	12
		4.0	73±2	16
		5.0	80±2	32
	C	1.0	77±2	7
		2.0	77±2	13
		3.0	79±2	20
		4.0	78±5	67
Goodyear Buna-S	A	3.0	78±2	4
	B	3.0	78±2	11
	C	1.0	77±1	7
		2.0	78±2	11
		3.0	78±2	18
		4.0	80±4	32
		5.0	82±6	72
Firestone Buna-S	C	3.0	80±2	16
Hycar OR-15	C	1.5	103±3	7
		3.0	104±6	21
Perbunan	C	1.5	94±4	9
		3.0	92±6	21
Butyl B-3	C	1.5	80±10	103[b]
Neoprene-GN	C	1.5	73±2	9
		3.0	78±4	18

[a] Data from previous publication[2].
[b] A few sulfur particles remained at the end of this period.

a thermocouple. The addition of sulfur was started after 10 minutes of milling, and required 2 minutes. Samples were removed and observed under a microscope every 2 minutes after this addition until solution was nearly complete, after which the observations were made every minute to determine when solution was complete.

The data on the time required for the solution of sulfur in elastomers on the mill rolls is given in Table I. The ratio of the rates of solution for three

FIG. 2.—Rate of solution of sulfur in elastomers during milling at 78° C. 1, crepe rubber with sulfur A; 2, GR-S with sulfur B; 3, crepe rubber with sulfur B.

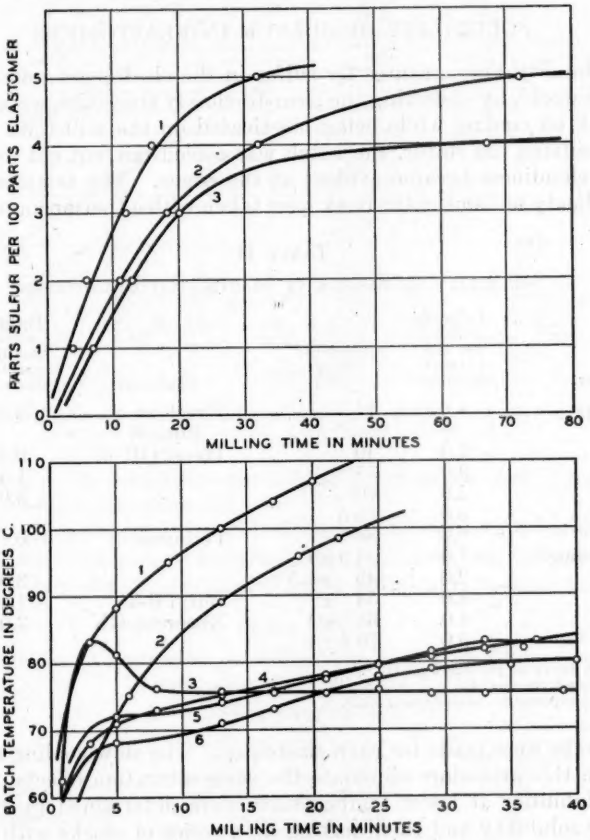

FIG. 3.—Heat build-up in elastomers during milling. 1, Hycar OR-15; 2, Perbunan; 3, crepe rubber; 4, Buna-S; 5, Neoprene-GN; 6, Butyl B-3.

parts of sulfur in Buna-S is approximately 1:3:5 for the A, B, and C grades, respectively. These data show the large influence of fineness on rate of solution of sulfur in rubber, as might be expected. The rate of solution of sulfur in natural rubber, Buna-S, and Neoprene-GN is about the same. The rate is appreciably slower for the Hycar OR-15 and Perbunan when the higher milling temperatures are considered. The solution rate of 1.5 parts of sulfur in Butyl rubber is very slow, since the temperature required for solution with this amount of sulfur was not reached. Plotted on Figure 2 are those values ob-

tained for natural crepe and Goodyear Buna-S, in which different grades of sulfur were studied.

Table I shows that the batch temperatures of the various elastomers on the mill varied somewhat. Since this was due to differences in internal friction in these materials, a study was made of the temperature variation of the batch during milling where all conditions were kept constant, except the type of elastomer used. The data are plotted in Figure 3. The equilibrium batch temperatures of the synthetic elastomers after considerable milling are higher than those obtained for natural crepe rubber.

SOLUBILITY OF SULFUR IN ELASTOMERS

The solubility temperatures for sulfur in the elastomers were obtained, as in previous work[1], by observing the clear-to-cloudy transition which takes place in the bank on cooling while being masticated on the mill rolls. After completely dissolving the sulfur, the batch was cooled but not cut on the moving rolls until cloudiness became evident at the edges. The temperatures of the clear and cloudy sections in the bank were taken with a thermocouple (Table II).

TABLE II

SOLUBILITY OF SULFUR IN MASTICATED ELASTOMERS

Elastomer	Parts of sulfur per 100 parts of elastomer	Solubility temp. (° C)	Elastomer	Parts of sulfur per 100 parts of elastomer	Solubility temp. (° C)
Natural crepe rubber[a]	1.0	14	Firestone Buna-S	3.0	52.5±1
	2.0	40	Hycar OR-15	0.3[c]	24.5±1
	3.0	55		1.5	71.5±2
	4.0	70[b]		3.0	92 ±1
	5.0	78.5			
	6.0	88	Perbunan	0.4[c]	24.5±1
Goodyear Buna-S	1.0[c]	24.5±1		1.5	56.5±1
	2.0	43 ±1.5		3.0	79.5±2
	3.0	54 ±1	Butyl B-3	1.5	93 ±3
	4.0	64.5±1	Neoprene-GN	3.0	54.5±1
	5.0	70.5±1			

[a] Data from previous publication (1).
[b] Redetermined, 68 ± 1° C.
[c] Constant-temperature room experiments.

Several checks were made for each elastomer. The slow cooling and constant agitation in this procedure eliminate the supersaturation effects of the sulfur.

The solubilities at lower temperatures were determined by first approximating the solubility and then making up a series of stocks with small differences in the dissolved sulfur content on each side of this approximated value. These stocks were then placed in constant-temperature rooms at different temperatures for long periods, and microscopic observations were made. The solubility values plot as straight lines on semilogarithmic paper, as shown in Figure 4.

The solubility of sulfur in some elastomers depend on the degree of mastication, increasing with increased breakdown until the limiting value shown in Table II is obtained. This characteristic was observed with natural crepe rubber and with Buna-S. Table III and Figure 5 record the change in sulfur solubility with mastication of these two elastomers, using 3 parts of sulfur.

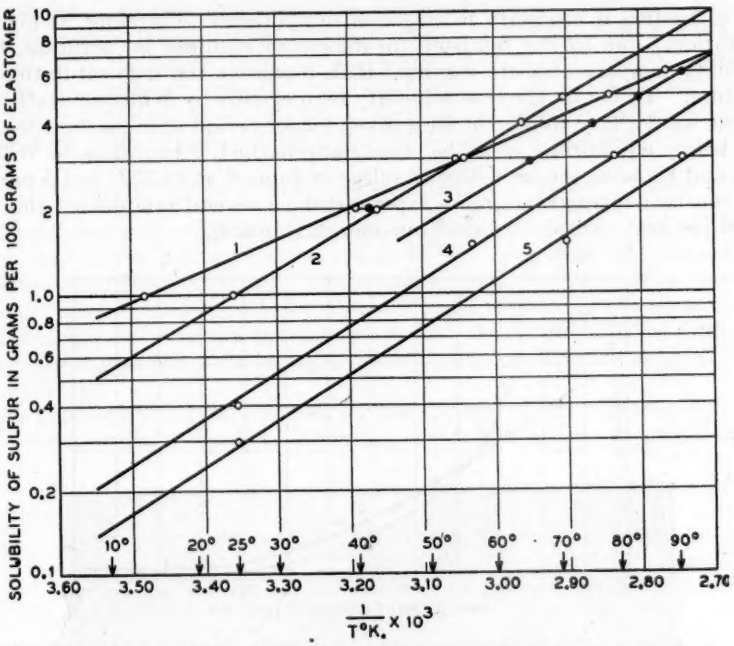

FIG. 4.—Solubility of sulfur in masticated elastomers. 1, Crepe rubber; 2, Buna-S; 3, Buna-S (Williams' results); 4, Perbunan; 5, Hycar OR-15.

Discrepancies of sulfur solubility values in rubber recorded in the literature may have been caused by this phenomenon.

Solubility values recently given by Williams[2] for Buna-S are lower than ours, except at the concentration of 2 parts sulfur. Considering his procedure and the poor miscibility of the polymer and sulfur noted, it is possible that a slower

TABLE III

EFFECT OF MASTICATION ON SOLUBILITY OF 3 PARTS SULFUR IN CREPE RUBBER AND BUNA-S

Elastomer	Time of mastication (min.) Before addition of sulfur	Time of mastication (min.) After addition of sulfur	Temperatures (° C) Max. batch, during milling	Temperatures (° C) Solubility or transition
Natural crepe rubber	10	40	81	65.4
		70		58.8
		110		56.2
		140		54.8
	5	30[a]	108	64.5
	170	60[b]	81	54.2
Goodyear Buna-S	10	25	80	62.1
		80		58.4
		125		56.6
		150		55.0
		185		54.5

[a] 8 minutes was required for complete solution of 3 parts of sulfur C in this slightly broken-down crepe at the high temperature.

[b] 50 minutes was required for complete solution of 3 parts of sulfur C in this highly broken down crepe; ordinarily 20 minutes (Table I) is sufficient.

rate of heating is necessary to establish equilibrium. Therefore, at high concentrations, due to the temperature difference required for solution, higher solubility temperatures are recorded than represent the true saturation temperature. To obtain the true solubility temperature by Williams' method, the sample would have to remain for a much longer period at a constant temperature before equilibrium could be closely approached. According to Williams' data and his plot, the solubility of sulfur in Buna-S at 24.5° C is 1.5 per cent. Our constant-temperature room experiments on several samples set this value at 1.0 per cent, established after one-month standing.

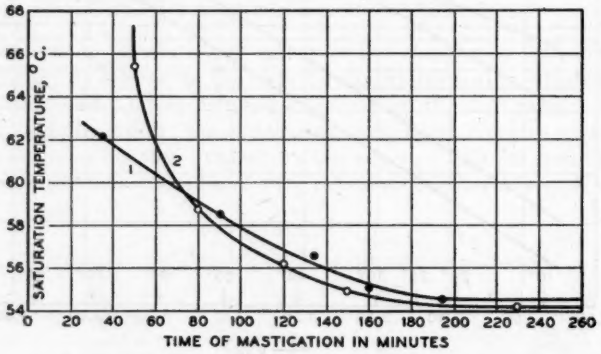

FIG. 5.—Effect of milling on solubility of sulfur in crepe rubber (curve 1) and in Buna-S (curve 2).

Since Williams master-batched the sulfur and Buna-S, an experiment was conducted to determine the effect of this variable on solubility. Goodyear Buna-S was master-batched with 15 parts of sulfur C at 125° C for 40 minutes, in accordance with Williams' procedure. The mixture was cloudy at the end of this time. Milling with cold water through the rolls was continued for 15

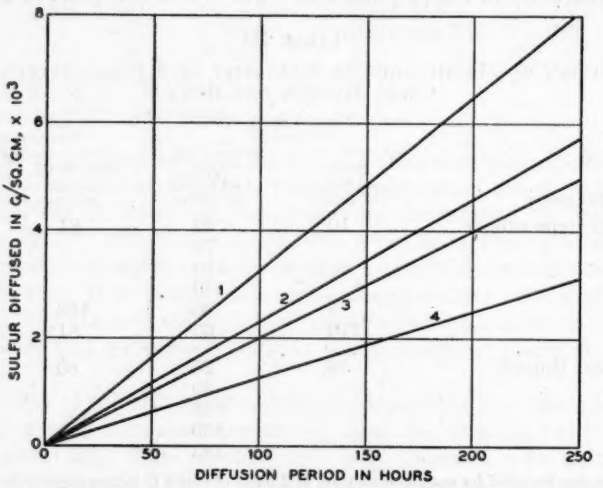

FIG. 6.—Rates of diffusion of sulfur through elastomers at 86° C. 1, Crepe rubber; 2, Buna-S; 3, Hycar OR-15; 4, Butyl B-3.

more minutes, at which time the batch temperature had fallen to 66° C. The master batch was then removed from the rolls. Additional Buna-S was added to a portion of the master batch so that the total mixture contained 3 parts of sulfur in 100 parts of Buna-S. This mixture was milled for 30 minutes at 80 ± 7° C; then cooling water was turned on to determine the saturation temperature. No difference from the value in Table II was obtained.

RATE OF SULFUR DIFFUSION THROUGH ELASTOMERS

The rates of sulfur diffusion through masticated Goodyear Buna-S, Hycar OR-15, and Butyl B-3 were measured at 86° C, using the diffusion cell and procedure described previously[1]. To obtain smooth sheets, the elastomer was milled 10 minutes and moulded between cellophane in a steam-heated press. Small amounts of volatile substances caused the early diffusion values of Buna-S and Hycar OR-15 to be high. Blanks were run, and the original values were corrected.

The experimental data obtained by the method of the previous investigation[1] were corrected to apply to the diffusion rate through a specimen 1 sq. cm.

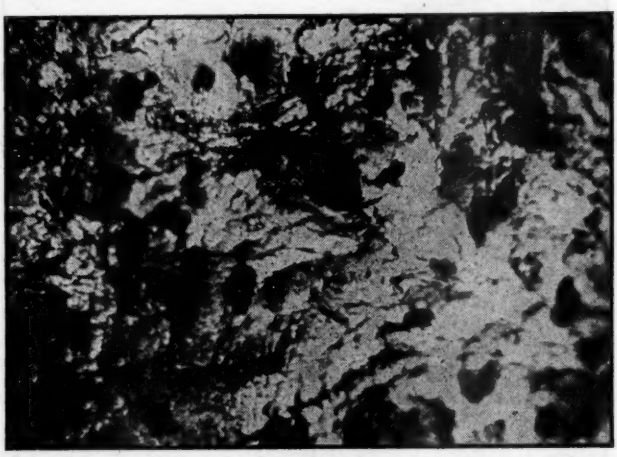

FIG. 7.—Undissolved sulfur in Buna-S (× 45).

in area and 0.030 cm. thick. The data obtained for the different elastomers are plotted in Figure 6.

The diffusion constant D, or specific diffusion rate, was calculated from Fick's law:

$$D = Nx/Atp$$

where N = weight of sulfur lost (grams)
x = thickness of rubber sheet (cm.)
A = area of rubber exposed to diffusion (sq. cm.)
t = time of diffusion (hours)
p = vapor pressure (mm.)

The calculated diffusion constants are given in Table IV. It is seen that the rates of sulfur diffusion in the elastomers studied decrease in the order: natural crepe rubber, Buna-S, Hycar OR-15, Butyl B-3.

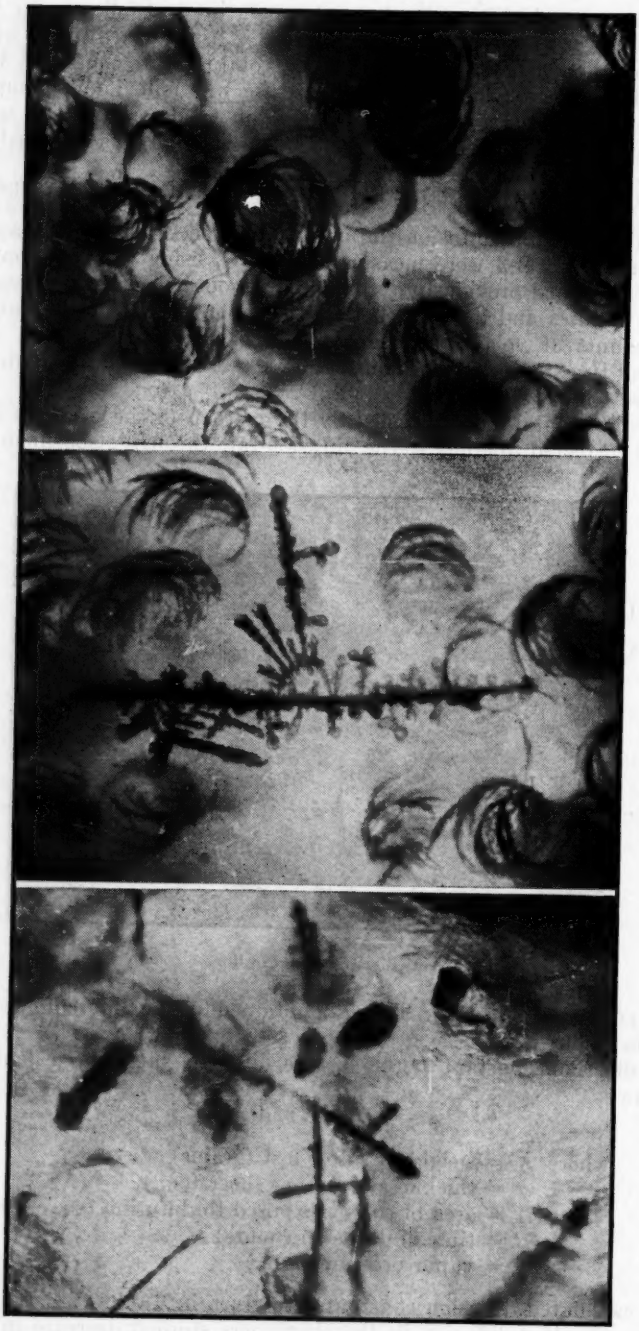

FIG. 8.—Transformation of sulfur in Buna-S from dendritic to rhombic form (×45).

TABLE IV

CALCULATED SULFUR DIFFUSION CONSTANTS FOR ELASTOMERS AT 86° C

Elastomer	Sheet thickness (cm.)	Average weight loss (g./hr.)	Diffusion constant D^b (g./hr./cm./mm. Hg)
Natural crepe[a]	0.0305	0.000160	4.4×10^{-4}
Buna-S	0.0312	0.000111	3.1×10^{-4}
Hycar OR-15	0.0429	0.000070	2.7×10^{-4}
Butyl B-3	0.0305	0.000064	1.7×10^{-4}

[a] Data from previous publication[1].
[b] Area of diffusion cell was 5.06 sq. cm. Vapor pressure of sulfur at 86° C is 2.2×10^{-3} mm. Hg[1].

CRYSTALLIZATION BEHAVIOR OF SULFUR IN ELASTOMERS

Microscopic observations made on a mixture of Goodyear Buna-S containing 3 parts of sulfur may be divided into separate categories. If, before complete solution, the sulfur-elastomer mix is allowed to cool and remain at room temperature, the excess dissolved sulfur will recrystallize on the undissolved particles, which results in the production of large crystals in the batch (Figure 7).

If, after complete solution, the mix is slowly cooled to and held at room temperature, the sulfur precipitates in the dendritic and rhombic states. Transformation from dendritic form into large rhombic crystals takes place on standing, as shown in Figure 8.

If, after complete solution, the mix is milled below its solubility temperature, the sulfur precipitates as numerous, very fine, uniformly dispersed rhombic crystals. This pattern (Figure 9), which causes the cloudiness visible to the

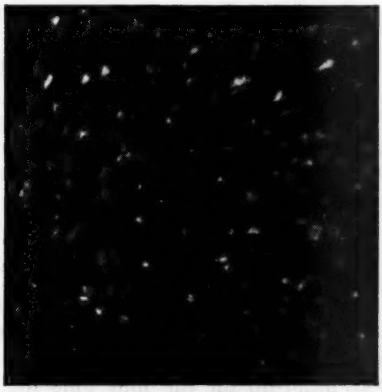

FIG. 9.—Fine sulfur crystals in Buna-S (oblique illumination, ×45).

naked eye, is retained on standing. Blooming is completely eliminated. Heating during vulcanization causes these very small crystals to redissolve quickly, and this is favorable for the formation of a homogeneous vulcanizate.

If, after complete solution, the mix is chilled in ice water, the sulfur precipitates in masses of dendrites. Short storage periods at room temperature do not alter this sulfur pattern, which dissolves quickly on heating, and yields a homogeneous vulcanizate.

Heterogeneous vulcanization involves the incomplete solution or local high concentration of sulfur or accelerators in rubber during vulcanization, as previously shown. With a micromould (Figure 10) it was possible to determine

comparative rates of resolution of different size sulfur crystals in natural rubber. The micromould was brought to a temperature of 141.5° C and loaded with the sample of crepe rubber containing the fine sulfur crystals previously described. Observations were then made under a microscope at a magnification of 40 diameters. These small crystals required only 1.5 minutes for complete

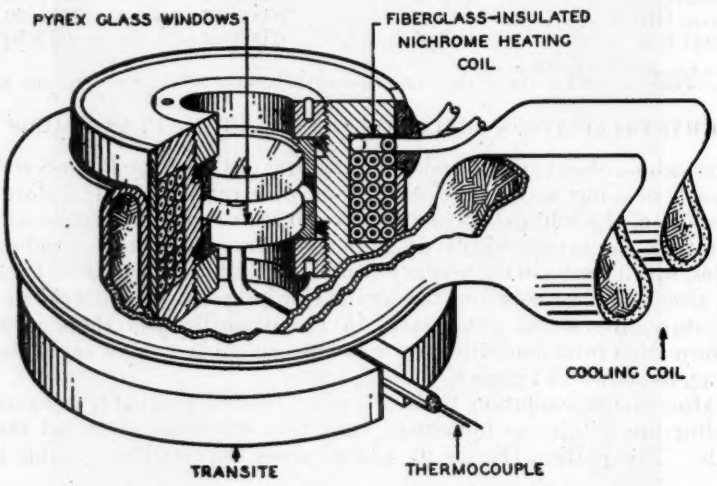

FIG. 10.—Micromold for observation of sulfur in elastomers during heating.

solution. The larger crystals previously described, which separated on standing at room temperature, required 13 minutes to dissolve at the same temperature, a difference of about ten times. It is this difference in rate of resolution, which depends on solubility, and the rate of diffusion of sulfur in the elastomer, that determine whether a heterogeneous or a homogeneous vulcanizate is formed.

CONCLUSIONS

1. The rate of solution of sulfur in various elastomers during milling depends on the temperature of the elastomer, the solubility and rate of diffusion of sulfur in the elastomer, the particle size and type of sulfur used, and the degree of breakdown of the elastomer.

2. The relative heat build-up on the mill rolls for each elastomer after 30-minute milling increases in the order: natural crepe rubber, Butyl, Buna-S, Neoprene-GN, Perbunan, Hycar OR-15. Conclusions as to extent of cross-linkage, mutual attraction of the chain molecules, and plasticity are indicated from data of this type.

3. The solubility of sulfur in the several elastomers increases with the degree of mastication, as shown in the cases of natural crepe and Buna-S, until a limiting value is obtained.

4. The specific diffusion rate of sulfur through various elastomers was determined. These rates of diffusion decrease in the following order: natural crepe rubber, Buna-S (GR-S), Hycar OR-15, Butyl B-3.

5. In synthetic elastomers the change in sulfur solubility with increase in temperature is greater than in natural rubber, the solubility is less at room

temperature, and the rates of diffusion are slower; therefore the possibilities of heterogeneous vulcanization with these elastomers are increased.

ACKNOWLEDGMENT

The authors are indebted to R. H. Walcott of the Stauffer Chemical Company for the particle-size analysis of the sulfur samples.

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THE COMPOUNDING OF HARD GR-S *

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Information on hard GR-S stocks has been limited so far to a paper by Cheyney[1]. This paper described the analytical characteristics and tensile properties of simple vulcanizates composed of GR-S and sulfur. It pointed out that GR-S vulcanizates increase in tensile strength as the sulfur content is increased from 0 through 35 per cent. This is opposite to the behavior of Hevea rubber-sulfur vulcanizates, which suffer a serious loss in tensile strength at intermediate sulfur concentrations.

The purpose of the work reported here was to gain information on the compounding of hard GR-S which could be used as a basis for devising technical stocks for specific applications. The authors were interested in finding the effects of sulfur content, type of pigment loadings, type of softener and type of accelerator on the tensile strength, ultimate elongation, flexural stiffness and hardness of hard GR-S vulcanizates. In addition, some indication of the softening point and impact resistance of hard GR-S vulcanizates was desired.

The study was made in a stepwise manner. First, the optimum amount of sulfur was determined. Using this amount of sulfur, the properties conferred by various pigments were found. Then, using the optimum amount of sulfur and the best pigment, the suitability of various softeners was found. Finally, using the optimum sulfur content, the best pigment loading and the best softener, the value of various accelerators was found.

PREPARATION FOR TESTING

Mixing was done on a cold 10-inch × 20-inch mill. The GR-S was broken down by passing it ten times between the rolls set at 0.02-inch opening. The mill was then opened to give a thicker band, and the sulfur was added. The sulfur was ground into the rubber by again tightening the rolls to give a 0.02-inch opening, and passing the batch through ten times. The batch was finished at a heavier gauge by rolling and cutting six times, and passing through endwise six times. At least 24 hours later, additional compounding ingredients, if any, were added. The batch was allowed to stand for another 24-hour period, and then refined by passing three times through a tight mill.

The stocks were given set cures, in the form of ⅛-inch thick sheets and ½-inch thick sheets, in a hydraulic press. The cures were just long enough so that the sheets had sufficient strength to be removed from the mould and

* Reprinted from *The Rubber Age* (New York), Vol. 54, No. 2, pages 129–133, November 1943.

were not too hard for cutting. A. S. T. M. tensile test-specimens[2] and ½-inch square bars, five inches long, were cut from the semicured sheets. These specimens were then given their final cure in open steam.

After final cure, the surfaces of the specimens were smoothed and squared by buffing. This buffing was done on a water-cooled machine.

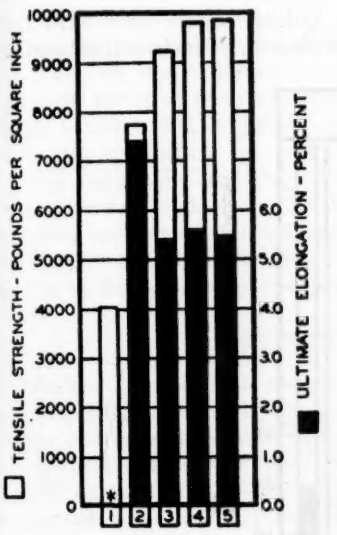

FIG. 1.—Effect of variation in sulfur content.

LEGEND

Symbol	Sulfur (parts per 100 GR-S)	Time	Cure temp.
1	20	26	307° F
2	30	8	307° F
3	40	19	287° F
4	50	14	287° F
5	60	11	287° F

* Ultimate elongation, 46 per cent.
** Rockwell hardness reading, minus 67.

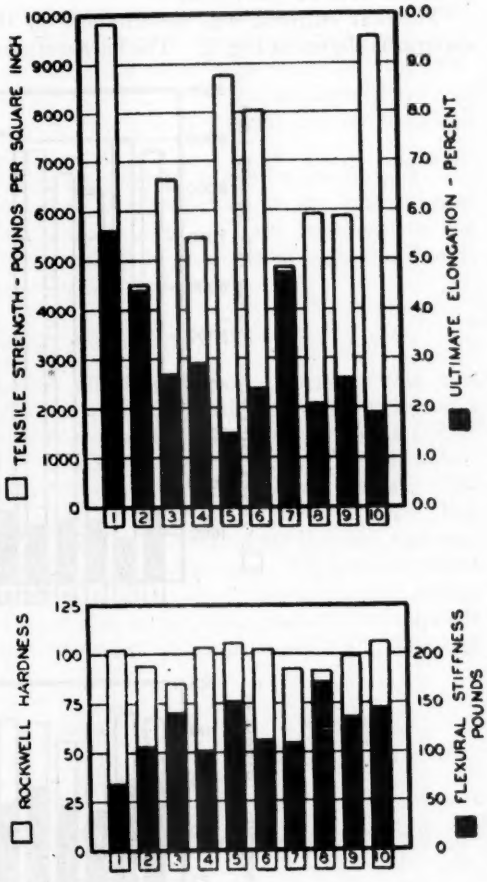
TENSILE STRENGTH - POUNDS PER SQUARE INCH
ULTIMATE ELONGATION - PERCENT
ROCKWELL HARDNESS
FLEXURAL STIFFNESS POUNDS
1 2 3 4 5 6 7 8 9 10

FIG. 2.—Effects of different pigments at 60-volume loading.

LEGEND

Symbol	Pigment loading	Cure at 307° F (hours)
1	No pigment (at 287° F)	14
2	Whiting	5
3	Hard clay	5
4	Ground silica	5
5	Semi-reinforcing black	4
6	Calcium silicate	3
7	Barytes	5
8	Magnesium silicate	5
9	Iron oxide	5
10	Channel black	2½

METHODS OF TESTING

Tensile testing was performed in accordance with the method recommended by the A. S. T. M. (6). The horizontal machine used for the tensile tests is shown in Fig. 1. The cure of each stock which gave the optimum tensile strength was selected for further tests. Each test result is the modal average obtained with 11 specimens.

Flexural stiffness was determined on the ½-inch square bars with the apparatus shown in Fig. 2. The bars were supported on ⅛-inch-radius bearing

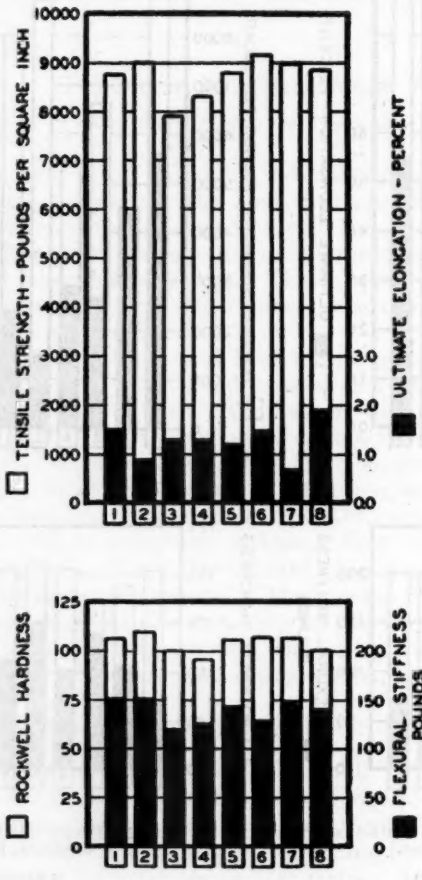

FIG. 3.—Effects of different softeners at 15-parts loading.

LEGEND

Symbol	Softener	Cure at 307° F (hours)
1	No softener	4
2	Cumar P-10	5
3	Pine tar	3
4	Petroleum residuum	3
5	Rosin oil	5
6	Barrett No. 10 oil	4
7	Guayule rubber resin	4
8	Naftolen-510	2½

edges separated by a distance of 4.0 inches, and were flexed by application of a load midway between the points of support. The load was applied by means of a pressure piece having a ⅛-inch-radius bearing edge. The load necessary to cause a deflection of 0.050-inch at the center of the beam was considered to be a measure of the stiffness of the hard rubber. The entire apparatus was supported on the weighing platform of a universal tester, by means of which the applied load was measured. The deflection was measured with a micrometer gauge. Each test result is the modal average obtained with five specimens.

Hardness was determined on ⅛-inch thick specimens with the Rockwell hardness tester as recommended by the A. S. T. M. The Rockwell hardness tester is illustrated in Fig. 3. Each test result is the modal average obtained with four specimens.

Softening point and impact resistance were determined by the A. S. T. M.-recommended methods. The impact test was performed on the simple-beam notched specimen (Charpy type) as shown in Fig. 4. Each test result is the modal average obtained with three specimens in the case of softening point, and with five specimens in the case of impact resistance.

EFFECTS OF SULFUR CONTENT

Before entering into a study of the effects of sulfur content, it was considered advisable to investigate the relative suitabilities of ordinary ground sulfur and micronized sulfur[3] from the standpoint of ease of dispersion in GR-S.

Two batches were prepared. One batch contained 50 parts of ground sulfur in 100 parts of GR-S; this sulfur was sifted through a 100-mesh screen. The other batch contained 50 parts of micronized sulfur in 100 parts of GR-S; this sulfur was not sifted. Within eight hours after sheeting off the mill, cut sections of the stocks were examined under the microscope. Photomicrographs of the cut sections showed better dispersion in the case of the micronized sulfur.

Further evidence in favor of micronized sulfur was obtained from tensile tests of the respective stocks after curing for 14 hours at 287° F. The test results were as follows:

Sulfur	Tensile strength lbs. per sq. in.	Ultimate elongation (percentage)
Ground	9250	5.9
Micronized	9760	6.8

In view of the benefits of micronized sulfur, this sulfur was used in all subsequent work with hard GR-S.

Batches containing 20, 30, 40, 50, and 60 parts of micronized sulfur, respectively, per 100 parts of GR-S were prepared. The stocks containing 20 and 30 parts of sulfur, respectively, were vulcanized at 307° F. The stocks containing 40, 50, and 60 parts of sulfur, respectively, were vulcanized at 287° F, because it was found that these stocks were blown when vulcanized at 307° F.

The cures for optimum tensile strengths are listed below Figure 1. The bar graphs show that 50 parts of sulfur yielded optimum properties. There was, however, little difference between the properties of the stocks containing 40, 50, and 60 parts of sulfur, respectively. It was decided to use 50 parts of sulfur in the remainder of the work.

A comparison was made of the properties of hard GR-S with those of hard

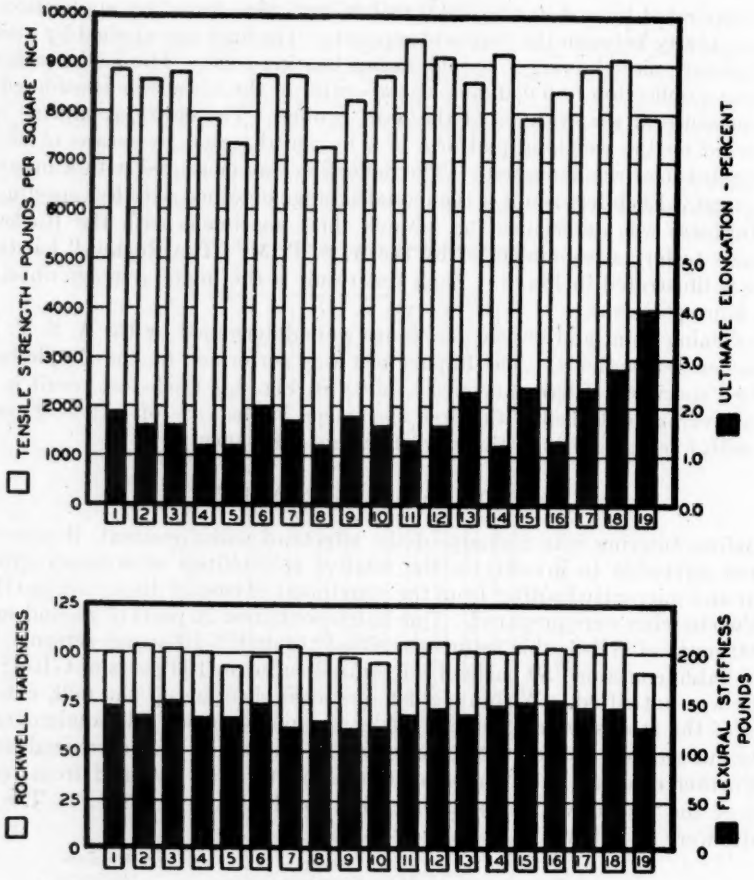

FIG. 4.—Effects of different accelerators.

LEGEND

Symbol	Accelerator	Proportion	Cure at 307° F (hours)
1	No accelerator	...	2½
2	Magnesia	5 vols.	1½
3	Hydrated lime	5 vols.	2
4	Litharge	5 vols.	2½
5	Zinc oxide	5 vols.	2
6	Vandex	2 pts.	2
7	Telloy	2 pts.	1½
8	A-77	2 pts.	1½
9	808	2 pts.	1
10	833	2 pts.	1
11	D.O.T.G.	2 pts.	1½
12	D.P.G.	2 pts.	2
13	Santocure	2 pts.	1½
14	Captax	2 pts.	2
15	Altax	2 pts.	2½
16	2-MT	2 pts.	2
17	Thionex	2 pts.	2
18	Methyl Tuads	2 pts.	2
19	Methyl Zimate	2 pts.	¾

Hevea rubber. Both stocks contained 50 parts sulfur and no other compounding ingredients. The data are given below:

	Hevea	GR-S*
Cure for optimum tensile strength (hours at 287° F)	8	14
Tensile strength (lbs. per sq. in.)	8560	9820
Ultimate elongation (percentage)	6.2	5.6
Rockwell hardness	90	102
Flexural stiffness (lbs.)	67	67
Softening point (° F)	145	144
Impact resistance (foot-lbs.)	0.45	0.23

* This was a different lot of GR-S from that used for the comparison of ground sulfur and micronized sulfur.

The Hevea stock was superior to the GR-S stock in curing rate and impact resistance. The Hevea stock was inferior to the GR-S stock in tensile strength and hardness.

EFFECTS OF PIGMENTS

The effects of different pigments at 60-volume loading on the properties of the 50-part sulfur stock are shown in Figure 2. These pigments generally shortened the cure to reach optimum tensile strength. This was particularly true in the case of the channel black loading. The cures are listed below the charts in Figure 2.

The pigments, of course, smoothed out the raw stocks. However, the stocks loaded with whiting and silica were difficult to handle because they possessed poor cohesive strength and therefore tended to crumble on the mill. Moreover, the stock loaded with channel black was somewhat stiff, and the stock loaded with calcium silicate was so stiff that it stopped the laboratory mill.

None of the loaded stocks quite equalled the base stock in tensile strength, ultimate elongation, or flexibility. The stocks loaded, respectively, with channel black, semi-reinforcing black, and calcium silicate, in order of preference, had the highest tensile strengths. The stocks loaded, respectively, with whiting and barytes had the highest ultimate elongations. The stocks loaded, respectively, with whiting, silica, calcium silicate, and barytes had the greatest flexibility. None of the loaded stocks were much harder than the base stock, and several were softer.

The authors were interested in obtaining a stock with strength and stiffness. Therefore, the semireinforcing black was selected as the loading for further work. Channel black was not selected because it gave such a stiff unvulcanized stock.

EFFECTS OF SOFTENERS

The effects of different softeners at 15-part loading are given in Figure 3. Some of the softeners, notably Naftolen-510, decreased the time to reach optimum tensile as is shown by the data below the charts.

Most of the raw stocks containing softeners had more tackiness than the base stock as determined qualitatively by hand test. The tackiness and Mooney plasticity of each stock are tabulated below:

Softener in stock	Tackiness	Mooney plasticity at 212° F
Cumar P-10	Fair	64
Pine tar	Good	64
Petroleum residuum	None	89
Rosin oil	Good	61
Barrett No. 10 oil	Fair	64
Guayule rubber resin	Fair	58
Naftolen-510	Poor	59

Rosin oil was an outstanding softener from the standpoint of tackiness. The raw rosin-oil stock also had fairly low plasticity and the vulcanizate had good tensile strength. The only disadvantage of rosin oil was its detrimental effect on the rate of cure.

The stock containing Naftolen-510 had higher ultimate elongation than the base stock and had, as mentioned above, a much faster rate of cure. Therefore, Naftolen-510 was chosen as the softener to use in the base stock for the accelerator comparison.

EFFECTS OF ACCELERATORS

The effects of numerous inorganic and organic accelerators on the base stock containing 50 parts micronized sulfur, 60 volumes (115 parts) semi-reinforcing black, and 15 parts Naftolen-510 are shown in Figure 4. Beneath the charts are listed the accelerators tested and the respective curing times to reach optimum tensile strength.

The fastest cure was obtained with Methyl Zimate. This stock, however, was impractical because it set up in storage. The next fastest cure was obtained with the aldehyde-amine accelerators, 808 and 833. These stocks did not set up in storage, and their vulcanizates possessed good tensile properties. Methyl Tuads did not speed up the cure very much, but its vulcanizate had good tensile strength and better elongation than all of the other stocks except the Methyl Zimate stock.

SUMMARY

A survey has been made of hard GR-S with regard to sulfur requirement and effects of various pigments, softeners, and accelerators on tensile strength, ultimate elongation, hardness, and stiffness. Of particular interest where the observations that hard GR-S had a higher tensile strength than hard Hevea rubber, and that hard GR-S did not undergo much loss in tensile strength when compounded with 60 volumes of channel black or semi-reinforcing black.

ACKNOWLEDGMENT

The considerable assistance given by Reed W. Rushton in this work is gratefully acknowledged.

REFERENCES

[1] Cheney and Robinson, *Ind. Eng. Chem.* **35**, 976 (1943).
[2] A. S. T. M., Tentative methods of testing hard rubber products, Designation D530-39T.
[3] Micronized sulfur is a very ground sulfur, produced by the Micronizer Processing Co., Inc.

LATEX COMPOUNDING OF GR-S *

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GR-S is utterly dependent on colloidal carbon for strength. Tensile strength, for example, is improved not twenty-five per cent as in Hevea, but six hundred per cent. In spite of this sensational improvement, GR-S develops only two-thirds of the strength of Hevea. It is evident, therefore, that a new compounding approach is required to raise the strength of GR-S to Hevea levels. It was largely with this thought in mind that, early in 1943, a study of the latex compounding of GR-S was launched in these laboratories.

In spite of the unpromising history of the reënforcement of Hevea by latex compounding, several factors favor latex compounding of GR-S. With the GR-S latex produced domestically, adequate supplies are assured for experimental and development work. With the failure of standard compounding to raise GR-S strength to Hevea levels, there is adequate room for further improvements in reënforcement. Latex compounding also presents a new angle of attack on the problem of the poor high-temperature properties of GR-S. Finally, the latex compounding approach offers an excellent means of reducing the total milling time in GR-S compounding.

The studies to date have shown that latex compounding improves GR-S, particularly in stress-strain properties and in resistance to hightemperatures. Typical changes and improvements in the properties of GR-S by latex compounding are demonstrated by the results of a carbon-loading study which is reported in detail. The results of other studies of different methods of preparation and different formulations are summarized briefly.

METHOD OF COMPOUNDING LATEX

In the normal method of compounding GR-S, following the practice used with Hevea, all the compounding ingredients, including carbon, are added to the dry polymer on the mill. In the latex method of compounding GR-S, part or all of the compounding ingredients is added to the latex before coagulation and milling. Two methods of adding the compounding ingredients to the latex were employed in the present studies. In one a slurry of carbon and all other ingredients was added to the latex; in the other an aqueous dispersion of carbon alone was added to the latex, with all of the remaining ingredients added on the mill.

The most satisfactory way to add compounding ingredients, particularly carbon, to latex is in the form of an aqueous dispersion. In the case of carbon, a good dispersion is prepared by milling approximately 30% carbon plus 5% dispersing agent (on the carbon) in tap water for 16 hours in a ball mill. This dispersion can be prepared more rapidly and simply in a colloid mill, the method which would be used in any practical application. Satisfactory dispersing agents include sodium hydroxide, ammonia, Darvan No. 1 and No. 2

* Reprinted from *The Rubber Age* (New York), Vol. 54, No. 5, pages 423–427, February 1944.

and Daxad No. 11, the latter preferred. By this method of addition a uniform nondusting black crumb results from the coagulation. The addition of dry carbon directly to latex has given a nonuniform dusty crumb after coagulation, which has unsatisfactory handling, processing and physical properties.

Various coagulants were tried, including sodium chloride, hydrochloric acid, salt-acid mixtures, zinc chloride and carbon dioxide. Zinc chloride and carbon dioxide were found to give better physical properties than the other coagulants, with zinc chloride preferred because of its handling and other advantages. It was also found that superior properties resulted when the coagulum was washed completely free of chlorides. For this purpose a fine crumb had a definite advantage, for example, over a mass coagulum.

The latex compounding method, finally worked out as most satisfactory for laboratory use, is described below. This method, in which the carbon alone was added at the latex stage, was used in the preparation of the carbon loading series described in detail later. In any practical application of the method, obvious changes would be made to simplify the somewhat involved laboratory procedure.

(1) A carbon dispersion is prepared by ball-milling, by the method previously described. (Colloid milling is preferred if equipment is available.)

(2) Sufficient carbon dispersion to give the desired loading of carbon on the rubber, and sufficient latex to give 400 grams of rubber, are weighed out separately.

(3) The latex is added to the carbon dispersion, with agitation. This takes about 3 minutes. The resultant mix is a uniform black liquid.

(4) This black latex mix is diluted with tap water to a rubber content of about 12 per cent. This is not necessary, but is done to assist coagulation in the laboratory, since manual agitation is inefficient.

(5) This diluted black latex mix is coagulated by adding the coagulant gradually, with vigorous agitation. A rubber-black coagulum is obtained in the form of a fine crumb. The aqueous phase is clear.

(6) The coagulated crumb is transferred to a large container, diluted freely, and allowed to stand for about one hour. This leaching step reduces the time needed to wash the crumb free of chlorides.

(7) The diluted batch is filtered with suction and washed with water until free of chlorides.

(8) The filter cake is pressed free of excess water, broken up by hand, and dried in shallow trays in the oven for 12–16 hours at 150° F. The uniformity and fineness of the dry crumb are shown in Figure 1.

(9) The dried crumb is sheeted out on a cold 2-roll mill (80° F) for 1–2 minutes and immediately compounded with the remaining ingredients. The total milling time, about 14–16 minutes, is considered sufficient for this compound.

In the preparation of a complete latex compound, the same procedure is used, except that the remaining ingredients are added to the latex via the carbon dispersion and are not added at the milling stage. The control for any latex-compounded stock is prepared from dry polymer, obtained preferably from the same batch of latex, by compounding completely in the normal manner on the mill. The milling time required for standard mill compounding is 16–20 minutes.

FORMULATION

The base compound used throughout these studies was as follows:

GR-S (solids)	100.
Carbon (EPC)	50.
Softener (Bardol)	7.5
Zinc oxide	5.0
Sulfur	2.0
Mercaptobenzothiazole	1.5
Antioxidant (BLE)	2.0
Dispersing agent	2.5

The GR-S, both latex and dry polymer, used throughout was Type I from the Naugatuck Chemical Division, U. S. Rubber Company. Type I contains the antioxidant shown in the base formula above. The latex was analyzed for solids content periodically to assure accurate formulations.

The carbon used throughout was Micronex W-6, an easy processing channel black (EPC). The loadings varied from 30 to 70 parts in the carbon loading series, the results of which are described in detail. In the other studies, the carbon loading was 50 parts.

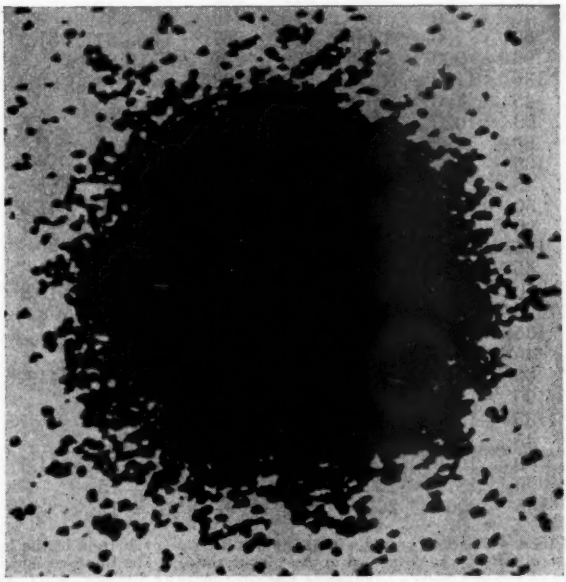

FIG. 1.—Black latex crumbs.

The dispersing agent was always present in the latex compound, but was not always added to the control milled compound. The presence of the dispersing agent in the control compound had a tendency to lower the properties slightly. In the carbon loading series, the dispersing agent was present only in the latex compounds.

Variations in formulation were found to produce the same changes in properties that might be expected in normal mill compounding. Increasing sulfur, for example, raised Shore hardness and rebound, but at the expense of

TABLE I

PROPERTIES OF LATEX AND MILL COMPOUNDED GR-S
(Detailed Test Data)

Compound	Carbon loading	Cure at 293° F (min.)	L-300	Tensile strength	Elongation (%)	Tensile product	Shore hardness (after 30 sec.)	Set (%)	Rebound (%)	Log R	Hot iron*
Latex	30	45	250	1850	850	157	41	25		10.4	>90″
		60	300	2100	785	165	44	21	59.0	9.9	>90″
		90	450	2125	675	144	47	16		9.9	7″
		135	550	1950	595	116	48	12		10.4	< 1″
Mill	30	45	400	1380	610	84	44	15		9.8	2″
		60	490	1475	570	84	47	14	59.0	9.7	< 1″
		90	540	1525	540	82	48	12		9.7	< 1″
		135	600	1490	515	77	48	9		10.1	< 1″
Latex	40	45	300	2250	840	189	44	31		9.1	>90″
		60	450	2500	755	189	46	30	54.4	8.6	>90″
		90	550	2875	720	207	50	26		8.7	28″
		135	700	2625	645	169	50	18		8.9	5″
Mill	40	45	510	2150	680	146	48	25		8.3	4″
		60	625	2300	640	147	50	21	55.9	8.2	2″
		90	790	2240	580	130	53	15		8.1	< 1″
		135	875	2090	515	107	54	11		8.7	< 1″
Latex	50	45	600	3190	770	246	51	37		7.9	77″
		60	700	3500	735	257	54	34	51.5	7.6	>90″
		90	900	3500	660	231	56	25		7.6	14″
		135	1190	3300	570	188	58	18		8.1	3″
Mill	50	45	780	2610	635	166	54	28		7.4	10″
		60	1020	2610	570	149	56	23	51.5	7.3	5″
		90	1190	2690	530	143	58	17		7.3	< 1″
		135	1225	2450	460	113	59	13		7.5	< 1″
Latex	60	45	690	2400	680	163	53	36		7.5	>90″
		60	1010	2780	605	168	56	29	47.3	7.4	>90″
		90	1175	3300	600	198	60	26		7.3	34″
		135	1360	3250	570	185	60	23		7.6	18″
Mill	60	45	910	2750	610	167	58	28		6.9	32″
		60	1300	2760	525	145	60	22	47.8	6.8	15″
		90	1440	3025	520	157	61	20		6.8	4″
		135	1675	2690	430	116	64	14		7.0	< 1″
Latex	70	45	1240	3210	600	193	62	36		6.8	75″
		60	1500	3125	530	166	64	28	44.6	6.7	39″
		90	1750	3075	475	146	65	22		6.8	16″
		135	1860	3050	445	136	66	19		7.0	15″
Mill	70	45	1310	3175	575	183	64	28		6.5	31″
		60	1660	2990	470	141	65	22	44.6	6.4	20″
		90	1870	2800	415	116	66	15		6.4	2″
		135	2090	2650	365	97	67	12		6.6	< 1″

* Hot Iron Method.—This test provides a simple quantitative evaluation of the heat tenderness, or thermal shortening, of GR-S. As developed in these laboratories ("The Improvement in Thermal Shortening and Fatigue of GR-S Treads", Columbian Carbon Company Bulletin, p. 11, 1943), a T-50 testpiece is stretched to a suitable elongation, is then placed in contact with a hot iron, and the time to failure in seconds is recorded. For tire compounds a stretch to 250 per cent and an iron temperature of 400° F are suitable. The hot iron preferred is a small electric patch heater, modified with a semicylindrical heater face.

elongation and tear. Increasing softener, from 7.5 to 12.5 parts, gave increased elongation and improved resistance to high temperature at overcures, with some sacrifice in tensile strength. Similar formulation tests were run with the zinc oxide and antioxidant varied. In summary, these various formulation tests demonstrate the suitability of the base compound shown above for latex compounding studies.

PHYSICAL PROPERTIES (CARBON LOADING SERIES)

Compared with mill compounded stocks, latex compounded stocks are characterized chiefly by higher tensiles and elongations and greatly improved heat resistance. These and other differences between latex and mill compounded stocks are shown in the series of carbon loading studies for which the detailed stress strain data are set forth in Table I. Properties at optimum cure are compared in Table II and Figure 2.

TABLE II

PROPERTIES OF LATEX AND MILL COMPOUNDED GR-S

(At optimum cure)

Compound	Carbon loading	Opt. cure at 293° F* (min.)	L-300	Tensile strength	Elongation (%)	Tensile product	Tear	Shore hardness	Rebound at 180 min. cure (%)	Set (%)	Log R	Hot iron
Latex	30	75	400	2145	725	156	Pass.	46	59.0	18	9.9	48″
Mill	30	75	510	1520	560	85	Pass.	48	59.0	13	9.7	1″
Latex	40	90	570	2870	685	196	Pass.	49	54.4	26	8.7	28″
Mill	40	60	640	2300	635	146	Poor	50	55.9	21	8.2	2″
Latex	50	70	760	3515	700	246	Fair	55	51.5	31.5	7.6	65″
Mill	50†	60	1020	2670	600	160	Pass.	56	51.5	23	7.3	5″
Latex	60	80	1180	3175	610	193	Fair	59	47.3	26.5	7.3	34″
Mill	60	80	1460	3010	535	161	Pass.	62	47.8	21	6.8	8″
Latex	70	45	1240	3210	600	193	Good	62	44.6	36	6.8	75″
Mill	70	45	1310	3175	575	183	Good	64	44.6	28	6.5	31″

* Optimum cures were chosen by hand test as the earliest cure of reasonable snap, with substantially unimpaired tear.

† Rubber Reserve Company (United States Rubber Company, its agent) reported the following specifications on the lot of GR-S used in this study:

Formula	WPB test compound
Optimum cure at 293° F	50 min.
Modulus	1110
Tensile strength	2780
Elongation	585

In this series, varied loadings of EPC carbon (Micronex W-6) were used in the base compound. The latex compounded stocks were prepared by the method described, in which only the carbon was added in the latex stage. In this series the mill compounded stocks did not contain the dispersing agent, and only in this respect did the formulas for the two compounds differ. The total milling times used in preparing these stocks are shown below.

Carbon (EPC) loading (parts)	Total time of milling (minutes)	
	Latex compound	Milled compound
30	14	16
40	15	16
50	15	16
60	15	17
70	16	19

It should be pointed out that the total time of milling for these latex compounds is relatively high because of the time required to add the softener on the mill.

If the softener is added to the latex via the carbon dispersion, the total milling time required is reduced materially. For complete latex compounds a total milling time of 10 minutes has been found adequate.

The results presented in Tables I and II and graphed in Figure 2 lead to the following conclusions.

(1) The reënforcement of GR-S is markedly improved by compounding in latex form, for all carbon loadings from 30 to 70 per cent by weight.

(2) Latex compounding of GR-S gives higher tensile strengths and better elongations than normal mill compounding at all carbon loadings. This advantage is particularly striking for the 50 per cent carbon compound where

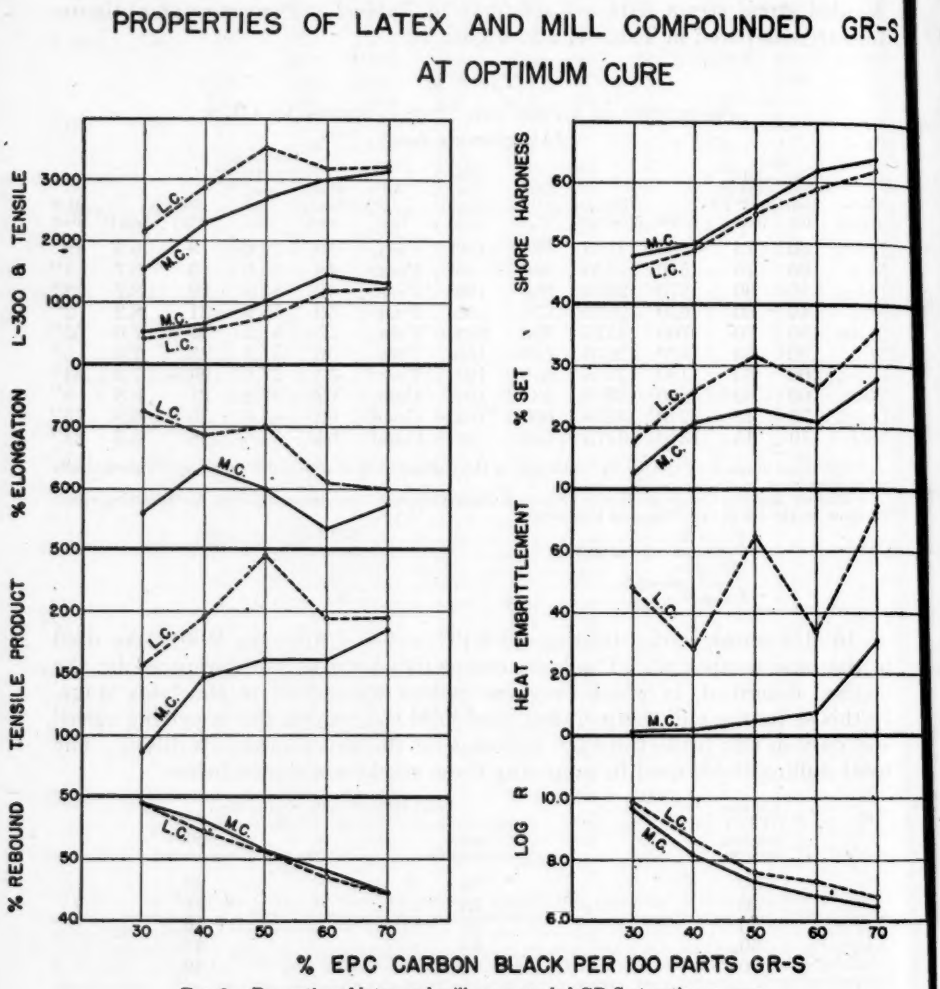

FIG. 2.—Properties of latex and mill compounded GR-S at optimum cure.

the tensile advantage is 845 lbs. per sq. in. and the elongation improvement is 100 per cent. The tensile product for this 50 per cent latex compound is 246, a value within the range shown by Hevea compounds.

(3) The more efficient carbon employment in latex compounding is so striking that the 40 per cent latex compound shows better tensile and elongation properties, combined with better rebound, than does the 50 per cent milled compound.

(4) The optimum tensile strength occurs at the 50 part loading for the latex compounds, while it is still increasing at 70 parts for the milled compounds.

(5) The latex compounded stocks show consistently lower modulus and higher subpermanent set. Rebound values are substantially equal for both compounds.

(6) The latex compounds cure only slightly more slowly on the average than the milled compounds.

(7) Heat resistance properties are markedly superior for the latex compounded stocks, determined by the hot iron test.

DISCUSSION

Complete latex compounding, that is, the addition of all the ingredients in the latex stage, was found to give the same improvements in GR-S compounds noted in the tests described, in which only carbon was added in the latex stage. In the few direct comparisons made between the two methods, the completely formulated latex compound showed substantially similar physical properties. The carbon latex method is preferred, however, because it permits greater flexibility in compounding. The results lead to the conclusion that, in latex compounding, the important step is the addition of carbon in the latex stage. For this step, well dispersed carbon is preferred.

The carbon dispersion in the black latex-crumb is improved by subsequent milling on the 2-roll mill. The time to add the remaining compounding ingredients on the mill (about 14–16 minutes) is usually sufficient to give satisfactory carbon dispersion. The degree of dispersion obtained is judged to be superior to that shown by the corresponding control milled compounds, on the basis of visual examination of the stocks.

The latex compounding method could, therefore, be defined as a new two-stage compounding process: (1) intimate mixing of latex and carbon in dispersion form, and (2) milling of the coagulated latex-carbon crumb, for less than normal time and at less than normal temperature, to give a final stock of superior carbon dispersion. The first stage makes possible the improved dispersion in the second stage. The beneficial effects from latex compounding result then from this two-stage process.

The effect of the improved dispersion resulting from this two-stage process would be to promote a more continuous carbon phase. This condition produces the following changes in the properties of latex compounded GR-S, which have already been noted:

(1) Improved reënforcement.

(2) Higher elongation and lower L-300, indicating less carbon flocculation.

(3) Higher set, which always improves both heat embrittlement and cut growth properties.

It seems probable that the beneficial effects of adding carbon to latex are also tied up with the well-known bad effect of heat, before vulcanization, on the properties of GR-S. In the normal milling method, GR-S is subjected to Banbury or mill heat before the carbon is dispersed in the rubber. On the other hand, in the latex method, carbon is mixed or dispersed into the latex without the development of heat. Subsequently the dispersed carbon may exert a protective action on the GR-S polymer during the coagulation, drying and milling stages, possibly by inhibiting to some extent excessive cross-linking of the polymer chains.

It is interesting to note also that the changes in properties of latex compounded GR-S lie definitely in the direction of Hevea properties. This is true of the improved stress-strain properties (tensile, elongation, T.P.), of higher subpermanent set, and of the remarkable improvements in heat resistance without loss in rebound.

SUMMARY

The more important findings in this study can be summarized as follows.

(1) A satisfactory technique has been worked out for compounding GR-S in latex form, either with carbon alone or with carbon plus the other compounding ingredients.

(2) Latex compounding of GR-S results in notable improvements in stress-strain properties.

(3) Latex compounding of GR-S results in outstanding improvements in heat resistance properties, without any loss in rebound.

(4) Latex compounding of GR-S results in lower modulus, higher elongation and higher subpermanent set. The increased set is significant, since it is accompanied by maintained rebound.

Besides giving improved quality, latex compounding offers practical advantages and possibilities. These are listed below:

(1) Latex compounding makes possible a reduction in the total milling time. This saving amounts to at least 10 per cent for carbon latex compounds and up to 50 per cent for complete latex compounds. The mixing time normally required in the Banbury is certainly not required.

(2) Latex compounding makes possible cooler handling of the GR-S. Since the carbon is added to the latex at room temperature, no high temperatures are involved during its incorporation as in Banbury mixing.

(3) Latex compounding makes possible cleaner handling of carbon, since it is added to the latex and is, therefore, mixed in the rubber before milling. If desired, the handling of carbon black could thus be transferred in toto to the polymer plants. This offers some interesting possibilities.

(4) Latex compounding to the black crumb stage, followed by sheeting and baling, should provide a convenient and economical means for shipping black, particularly for transoceanic deliveries. There would also be important savings in containers.

(5) The black latex crumb may provide a convenient form of compounded GR-S for extrusion and related operations.

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EXPERIMENTS ON SYNTHETIC RUBBERS OF THE BUTADIENE TYPE *

II. MECHANICAL AND ELECTRICAL PROPERTIES OF BUNA EBONITES

J. R. Scott

INTRODUCTION

The experiments described here were designed to examine the properties of ebonites made from various kinds of Buna synthetic rubber, including Buna-85, Buna-115, Buna-S and Buna-N.

All Bunas are said[1] to form ebonites by vulcanization with the normal amount of sulfur, Buna-85 and Buna-115 giving the best products. The resulting ebonites are stated to have much higher plastic yield temperatures than ordinary ebonite, figures quoted ranging from 100° to 175° C by the Martens test[2], compared with 70° to 90° C for natural-rubber ebonites. It may be added that Russian butadiene rubber likewise is claimed[3] to give ebonites with much higher yield temperatures, namely, up to 160° C by a Vicat needle test, than ordinary ebonites, which give about 93° C. On the other hand, Buna ebonites are relatively brittle[4]. The electrical properties of these ebonites are said to be good[5], and in this connection it should be noted that soft vulcanizates made from Buna-85 and Buna-115 have lower power factors than those made from natural rubber[5]. Buna ebonites are more resistant than ordinary ebonite to attack by chemicals and to the swelling action of liquids such as benzene and nitrobenzene[4].

The present report deals with certain properties of Buna ebonites, *viz.*, plastic yield, cross-breaking strength, impact strength, radio-frequency permittivity and power factor.

EXPERIMENTAL

The mixes examined were as follows:

	A	B	C	D	E	F
Buna-85	100	...	...	...	...	...
Buna-115	...	100	100	100	...	...
Buna-S	...	...	...	...	100	...
Buna-N	...	...	...	...	...	100
Sulfur	47	35	47	59	47	47

The proportion 100:47 corresponds to the 68:32 ratio needed to form the compound C_5H_8S from natural rubber. This proportion was used for most of the mixings because it is stated[1] that Bunas require the same proportion of sulfur as natural rubber to form ebonite. Since, however, Buna-85 and Buna-115 are polymers of butadiene, they should form the compound C_4H_6S, provided that one double bond per butadiene unit is available (this may not be

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the case, however, since the butadiene polymers are stated to be partially cyclized[6]). As the rubber-sulfur ratio in C_4H_6S is 100:59, these proportions were used in Mix D. Mix B was included to show the effect of using a low sulfur ratio.

The mix made with Buna-N was found to be very stiff and difficult to work on the mill.

The stocks were given a preliminary moulding in a platen press, using moulds 10 in. × 10 in. × 0.22 in. and a heating period of 50 minutes at 155° C. The moulded sheets were then transferred to thinner moulds (0.20 in. thick), to allow for shrinkage during vulcanization, and vulcanization was completed in an autoclave press at 155° C, the moulds being arranged in a pile with distance pieces between them to permit steam to circulate. Some of the stocks did not mould well, and for this reason it was not possible in all cases to obtain satisfactory specimens for the mechanical tests; although the results are thus rendered incomplete, they suffice to show clearly how the properties of Buna ebonites compare with those of ordinary ebonite. Mix F (Buna-N) proved to be especially difficult to mould.

The vulcanizing periods given in the tabulated results are the total equivalent periods at 155° C, including moulding and rises in the platen press and autoclave press.

The methods of testing were as follows:

Plastic Yield.—Torsion method[7] of the Research Association of British Rubber Manufacturers, using an improved apparatus. The results, which are mean values for duplicate specimens, are expressed as the angle of twist of a specimen 75 mm. long and 5 × 15 mm. cross-section, after subjection to a torque of 75 g.-cm. for 30 minutes.

Cross-Breaking Strength and Elongation.—Three-point loading method, using specimens 75 mm. long, 25 mm. wide, and of thickness equal to that of the moulded sheet, *i.e.*, about 5 mm., the distance between the supports being 50.8 mm. Full details of the method have been described in a previous report[8]. Six specimens were tested and the results averaged after excluding any obviously abnormal low figures.

Impact Strength.—Both notched and unnotched specimens were tested by a falling-weight machine. The width of the specimens was equal to that of the moulded sheet, and the depth, *i.e.*, dimensions parallel to direction of blow, 12.7 mm., this being measured to the base of the notch in the case of notched specimens. The notch was 6.3 mm. deep, the base being rounded to a diameter of 1.6 mm. The specimens rested on supports 50.8 mm. apart and were struck in the center. Each specimen was struck with successively increasing blows until it broke[9]. Twelve specimens were tested and the results averaged after rejecting abnormally low figures.

Permittivity and Power Factor.—Tests were made by the National Physical Laboratory. Most of the measurements were carried out with a frequency of 1 million cycles per second, but a few additional tests were made at 800 cycles per second.

Plastic Yield

Table I gives the plastic yield data, together with these of two rubber-sulfur ebonites:

X:72:28 rubber-sulfur, vulcanized for 5 hours at 155° C.
Y:65:35 rubber-sulfur, vulcanized for 5 hours at 155° C.

The tabulated values were read from smoothed curves plotted from the experimental data.

TABLE I

Mix and vulcanization (hours)	Plastic yield (twist, in degrees) at temperature (° C)											
	40	50	60	70	80	90	100	110	120	130	140	150
A												
3	0.8	1.8	3.1	4.4	5.1	5.6	6.0	6.3	...	...	...	...
4	...	0.2	0.4	0.9	1.8	2.6	3.4	3.9	4.2	4.5	4.0	...
6	...	...	0.2	0.2	0.2	0.4	0.4	0.5	0.9	1.3	1.4	1.5
B												
3	0.8	1.6	3.7	4.9	6.0	6.8	7.1	7.3	...	...	...	...
4	...	1.4	2.4	3.7	4.9	5.9	6.4	7.0	7.6	7.9	8.3	...
11	...	...	0.3	0.3	0.5	0.8	1.2	1.8	2.6	3.3	3.8	3.7
C												
3	0.4	0.4	0.8	1.2	2.0	2.7	3.3	3.7	...	...	...	...
4	...	0.2	0.3	0.6	0.9	1.3	1.8	2.2	2.6	2.9	3.1	...
6	0.2	0.2	0.2	0.3	0.3	0.3	0.4	...	...	...	...	...
11	...	...	0.1	0.1	0.2	0.2	0.2	0.3	0.4	0.5	0.6	0.7
D												
3	0.2	0.2	0.3	0.5	0.9	1.4	1.8	2.3	...	...	...	...
4	...	...	...	0.2	0.3	0.4	0.6	0.8	0.9	...	...	...
6	...	...	...	...	0.1	0.2	0.3	0.3	0.3	...	...	...
11	...	...	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
E												
3	1.1	2.7	4.5	5.8	6.5	6.9	7.2	8.2	...	...	...	...
11	...	...	...	...	...	...	0.2	0.4	0.9	1.8	2.6	3.6
F												
3	0.3	0.3	0.4	1.0	3.8	6.7	8.6	10.5	...	...	...	...
4	...	0.1	0.1	0.2	0.2	0.3	0.6	1.8	4.6	6.5	8.5	...
6	0.1	0.1	0.1	0.1	0.1	0.1	0.1	...	...	...	...	...
11	...	...	...	...	...	...	0.1	0.2	0.2	0.2	0.4	1.4
X	...	0.2	0.4	0.9	8.4	14	15	16	...	...	...	...
Y	...	...	...	0.2	0.6	5.5	12	14	...	...	...	...

It is at once evident that the Buna ebonites give much smaller plastic yields, at least at the higher temperatures, than do the ordinary ebonites, and that the yield does not increase so rapidly with rise of temperature. In many cases, indeed, it is not possible to distinguish, on the temperature/yield curve, the relatively steep straight portion which is always present in the case of ordinary rubber-sulfur ebonite and which is used to determine the "yield temperature" by extrapolation back to the temperature axis[7]. Only with the 3 and 4 hour vulcanizates of Mix F is this straight part of the curve sufficiently well-defined to enable its slope and the yield temperature to be determined with any accuracy. In some other cases the curve approaches the normal type, and estimates of the yield temperature and slope have been made, though the figures must be accepted with some reserve (Table II). The slope figures, however, do show very clearly how slow is the increase of plastic yield with temperature, compared with that observed with ordinary ebonite.

As in natural rubber ebonite, increasing the proportion of sulfur (Mixes B, C, D) reduces the yield at any given temperature (Table I), reduces the slope, and raises the yield temperature.

Comparing the 11-hour vulcanizates of the mixings containing 47 parts of sulfur, and considering the yields at the highest temperature, 150° C, the following order of merit is obtained:

C	(Buna-115)	0.7° yield
F	(Buna-N)	1.4° yield
E	(Buna-S)	3.6° yield

Mix A (Buna-85) would probably be somewhere near C. As far as resistance to deformation at high temperatures is concerned, therefore, the results confirm the statement[1] that Buna-85 and Buna-115 give the best results.

TABLE II

Vulcanization	Yield temperature (° C)				Slope (degrees/10° C)			
	3 hrs.	4 hrs.	6 hrs.	11 hrs.	3 hrs.	4 hrs.	6 hrs.	11 hrs.
A	37	60	100	...	1.3	1.0	0.4	...
B	44	40	...	85	2.5	1.2	...	0.7
C	55	70	...	...	0.8	0.5	...	...
D	65	74	...	...	0.6	0.2	...	...
E	36	...	...	115	1.8	...	...	1.0
F	69	103	...	145*	3.7	2.7	...	...
X			73				11.5	
Y			83				8.2	

* Assuming same slope as for 4-hr. vulcanizate.

It appears that, to bring out the best heat-resistance in the Buna ebonites, a vulcanization of 6 hours or more at 155° C is required.

The curves obtained by plotting plastic yield against period of application of the torque, at a constant temperature, are of the same general form as those found with ordinary ebonite[7].

CROSS-BREAKING STRENGTH AND ELONGATION

Table III gives the cross-breaking strength and the apparent breaking elongation, calculated from the breaking load and maximum deflection of the specimen by the formulas previously given[8].

TABLE III

Vulcanization	Cross-breaking strength (kg. per sq. cm.)				Elongation (%)			
	3 hrs.	4 hrs.	6 hrs.	11 hrs.	3 hrs.	4 hrs.	6 hrs.	11 hrs.
A	820	935	465	...	13.5	9.9	3.1	...
B	560	555	...	780	10.0	9.1	...	8.2
C	450	...	...	475	5.3	...	...	5.6
D	415	490	335	415	6.0	5.6	4.5	4.3
E	...	...	...	540	...	...	...	7.1
F	...	605	650	700	...	4.6	5.6	5.4

All the cross-breaking strengths are considerably lower than those of ordinary rubber-sulfur ebonites, which range from about 1300 to 1500 kg. per sq. cm. Most of the elongations also are lower, ordinary ebonites (excluding very undervulcanized ones) giving from 10 to 15 per cent elongation.

It is clearly not possible from the data in Table III to assign any reliable order of merit to the various mixes. A and F (Buna-85 and Buna-N), how-

TABLE IV

IMPACT STRENGTH (KG.-CM. PER SQ. CM.)

Vulcanization	Unnotched				Notched			
	3 hrs.	4 hrs.	6 hrs.	11 hrs.	3 hrs.	4 hrs.	6 hrs.	11 hrs.
A	17	9.6	...	...	2.7	2.0	...	...
B	13	13	...	3.9	3.4	3.4	...	1.8
C	8.1	...	...	4.3	2.1	...	...	0.6
D	6.1	3.6	1.9	...	2.1	1.4	1.7	...
E	...	11	...	...	...	...	...	...
F	...	...	6.9	...	...	1.4	2.0	...

ever, appear to give the best strength; the low-sulfur Buna-115 Mix (B) also is good, but increasing the sulfur (Mixes C and D) appears to reduce the strength as well as the elongation. In ordinary rubber mixes, increasing the sulfur raises the cross-breaking strength.

IMPACT STRENGTH

The impact strengths of unnotched specimens are much less than those of natural rubber-sulfur ebonites, for which values of 40–70 kg.-cm. per sq. cm. have been found. The notched specimens, however, generally give values of the same order as those for ordinary ebonite, namely 1.7–4.0 kg.-cm. per sq. cm.

Differences between the various mixes are not clearly shown, except that in the series B, C, D increasing the sulfur content generally reduces the impact strength, as is the case also with natural rubber ebonites.

Impact strength generally decreases with advancing vulcanization; in the case of unnotched specimens, this effect is much more pronounced than with ordinary ebonite.

PERMITTIVITY AND POWER FACTOR

No tests were made on the Buna-N ebonites (Mix F), because this type of Buna does not possess good electrical properties.

The National Physical Laboratory made measurements of permittivity and power factor at a frequency of 1 million cycles per second, using alternating

TABLE V

Hours	Permittivity	Power factor (%)
3	2.73	0.39
11	2.78	0.56
B 3	2.69	0.56
6	2.72	0.59
C 3	2.76	0.48
6	2.79	0.61
D 3	2.82	0.46
6	2.85	0.57
E 4	2.89	0.74
6	2.91	0.88

voltage of sine-wave form. The results are given in Table V for a temperature of 20° C and ordinary atmospheric humidity conditions.

In most cases the permittivity is only slightly below that of ordinary rubber-sulfur ebonite, *viz.*, 2.80–2.88, but the power factor is considerably lower, ordinary ebonites giving values between 0.77 and 0.95 per cent.

Both permittivity and power factor increase as the period of vulcanization is lengthened; natural rubber ebonites show the same effect in the case of power factor, but not always with permittivity.

In the mixings containing 47 parts of sulfur per 100 of Buna, both power factor and permittivity are lowest with Buna-85 (Mix A) and highest with Buna-S (Mix E), Buna-115 (Mix C) being intermediate; this further confirms the statement[1] that Buna-85 and Buna-115 give the best results. Increasing the sulfur content in the series B, C, D increases the permittivity, but, if anything, reduces the power factor, the means for the respective mixes being 0.575, 0.545, 0.515; these effects are in the same direction as those observed with natural rubber ebonites.

Mix A gave higher values for power factor and permittivity at 800 than at 1 million cycles per second, the values for the lower frequency being as follows:

		Permittivity	Power factor (%)
A	3 hr.	2.80	0.47
	11 hr.	2.85	0.68

A natural rubber ebonite containing the same proportion of sulfur as Mix A shows a similar change in permittivity on passing from 1 million to 800 cycles per second, but the power factor decreases, so that, at 800 cycles per second, it has a value (0.58 per cent) similar to that of the Buna-85 ebonite.

It is noteworthy that, whereas polystyrene has an extremely small power factor (about 0.03 per cent), the copolymer of styrene and butadiene (Buna-S) gives ebonite with a higher power factor than that made from polymerized butadiene (Buna-85 or Buna-115). It is possible, of course, that this might be due to the presence in Bunas of some electrolyte or polar substance.

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III. BUNA EBONITES: DEGREE OF VULCANIZATION, AND RESISTANCE TO WATER, ORGANIC LIQUIDS AND LIGHT

INTRODUCTION

No information appears to have been published hitherto on the tendency of Buna ebonites to absorb water, although this is an important point in electrical application, or on their behavior during exposure to light, except a statement[1] that the surface behaves like that of natural rubber ebonite, due to the formation of sulfuric acid. The resistance of Buna ebonites to organic liquids is claimed to be very good[2], but the only data in support of this that have been found are for swelling in nitrobenzene[3].

EXPERIMENTAL

The ebonites examined had the following compositions:

	A	B	C	D	E	F
Buna-85	100	...	...	...	...	...
Buna-115	...	100	100	100	...	...
Buna-S	...	...	...	...	100	...
Buna-N	...	...	...	...	...	100
Sulfur	47	35	47	59	47	47

The reason for the particular sulfur ratios used is explained in Part II[4]. Samples in the form of sheets 5 mm. thick were press-vulcanized at 155° C.

Combined Sulfur Content

To determine how much of the added sulfur had combined with the Buna, the sulfur in the acetone extracts of the ebonites was estimated by the bromine oxidation method, with the results (means of duplicates) given in Table I.

Table I

Mix	Period of vulcanization (hrs.)	Acetone extract (%)	Sulfur in in extract (%)	Corrected acetone extract* (%)
A	6	1.6	0.35	1.25
B	11	0.85	0.05	0.8
C	6	0.95	0.15	0.8
C	11	0.75	0.10	0.6
D	6	1.05	0.45	0.6
D	11	0.75	0.15	0.6
E	11	2.35	0.15	2.2
F	11	3.9	0.40	3.5

* Acetone extract less the sulfur contained in it.

Judging by the figures for sulfur in the acetone extracts, the proportion of free sulfur appears generally to be lower than in natural rubber ebonites (see, *e.g.*, Table II). This is partly ascribable to the fact that butadiene has a lower molecular weight than isoprene, so a butadiene polymer can take up more sulfur than the same weight of natural rubber, assuming one double bond per

Table II

Period of vulcanization (hours)	Buna		Natural rubber	
	Mix	Free sulfur	Mix	Free sulfur
6	A (100:47)	1.1	100:37	1.3
6	C (100:47)	0.5	100:37	1.3
11	C (100:47)	0.35	100:37	0.7
6	D (100:59)	1.2	100:47	5.0
11	D (100:59)	0.45	100:47	5.0

Free sulfur, as percentage of total sulfur in mix.

butadiene or isoprene unit. The following considerations, however, show that this is not a complete explanation. Taking into account the difference in molecular weight, the 100:35, 100:47, and 100:59 Buna-sulfur mixings correspond to 100:28, 100:37, and 100:47 rubber-sulfur mixings, respectively. From previous data it is possible to estimate what proportion of the sulfur would remain uncombined in the last two of these mixings; this is shown in

Table II in comparison with corresponding figures for the ebonites made from butadiene polymers.

In every case the butadiene polymer takes up the sulfur more completely than natural rubber, this difference being especially marked in the mix (D) containing most sulfur.

A further point of interest is that in the 11-hour vulcanizate of mix D there is almost exactly 1 atom of combined sulfur per molecule of butadiene. If, as has been stated[5], butadiene polymers are partially cyclized, there would be less than 1 double bond per butadiene molecule; the present results therefore show either that more than 1 atom of sulfur per double bond becomes combined, or that the structure becomes "uncyclized" during the formation of ebonite, unless indeed the assumption of a cyclized structure is incorrect.

The combined sulfur content of the Buna-N ebonite (F) is very close to the theoretical maximum value for a copolymer of 75 per cent butadiene and 25 per cent acrylonitrile (the proportion indicated by analysis[6]; assuming 1 double bond per butadiene molecule and 1 atom of combined sulfur per double bond.

Water Absorption

This was determined by the method of the Research Association of British Rubber Manufacturers[6], the powdered ebonite, previously dried, being exposed to air of 97.2 relative humidity at 25° C, and the increase in weight determined periodically by weighing the sample while still in the controlled atmosphere. The ebonite was finally dried again in air of 0 relative humidity. The weight increase was used to calculate the amount (cc.) of water absorbed by 100 cc. of ebonite, this being termed the "apparent water absorption" (apparent because any weight increase due to oxidation would be reckoned as water). The mean results of duplicate tests are given in Table III; all the ebonites used were vulcanized for 11 hours at 155° C.

Table III

	Apparent water absorption (percentage)					
	97.2% relative humidity				0% relative humidity	
Mix	1 day	4 days	5 days	6 days	5 days	7 days
A	1.4	1.35	1.25	1.3	0.18	0.18
B	1.5	1.45	1.5	1.5	0.22	0.23
C	1.05	1.05	1.15	1.15	0.17	0.17
D	0.82	0.86	0.88	0.93	0.14	0.16
E	0.52	0.59	0.62	0.64	0.13	0.13
F	3.35	4.05	4.25	4.5	1.0	1.0

Even if it is assumed that the apparent residual absorption after drying is really due to oxidation, and hence should be subtracted from the 97.2 per cent relative humidity absorption figures, the results for all except the Buna-S ebonite (E) are higher than results previously obtained for ebonites made from washed smoked sheet, namely, 0.45–0.50 per cent. This greater tendency to absorb water will to a greater or less extent offset the superiority of Buna ebonites A-D in electrical properties[4], at least in cases where the ebonite is exposed to damp conditions during use.

Absorption is especially high with the Buna-N ebonite (F), an unexpected result in view of the fact that a soft vulcanizate made from a similar mixed polymer, Perbunan, absorbs less water than a natural rubber vulcanizate[7].

It is possible that the emulsifying agents used in making these emulsion polymers may be responsible for the anomalous water-absorption effects.

In the series B, C, D, water absorption decreases with increasing sulfur content of the mix, an effect not evident in a similar series of rubber-sulfur mixes.

Swelling in Organic Liquids

This was determined by immersing a piece of the ebonite 20 × 20 × 5 mm. in the liquid, and weighing it periodically, the swelling, *i.e.*, volumes of liquid absorbed by 100 volumes of ebonite, being calculated from the weight increase and the densities of the liquid and ebonite. In some cases a small negative "swelling", due to extraction of soluble substances, was recorded. The liquids used were: benzene (A.R.), petroleum ether (density 0.670 at 25° C), aviation gasoline (density 0.751 at 25° C), transformer oil (density 0.87 at 25° C), carbon disulfide, and nitrobenzene. All tests were made at 25° C, except those with transformer oil, for which 70° C was used. The complete results are given in Table IV. Mixes B–F were vulcanized 6 hours, and A 11 hours, at 155° C.

To facilitate comparison of the ebonites among themselves and with natural rubber ebonites, the swelling after a definite period is shown in Table V. In connection with the latter Table it should be noted that in some cases the Buna ebonites had not reached their maximum swelling at the end of the experiment, even when this continued for some months. This is the case notably with Buna-115 (B) in petrol, petroleum ether, and nitrobenzene, Buna-115 (C) and Buna-S (E) in benzene, and Buna-N (F) in carbon disulfide. The comparison indicated by the figures in Table V is, therefore, one of essentially practical, rather than theoretical significance.

It is at once evident from Table V that Buna ebonites are generally much more resistant to the swelling action of benzene and nitrobenzene than is natural rubber ebonite, but there is a less marked superiority with carbon disulfide. Petroleum ether, gasoline, and transformer oil generally have no appreciable swelling action, the only exception being the low-sulfur Buna-115 ebonite (B) in petroleum ether and gasoline.

In series B, C, D, the swelling nearly always decreases with increasing sulfur content of the mix, just as in natural rubber ebonites.

Among the 100:47 Buna-sulfur ebonites, the greatest swelling is shown by Buna-115 and Buna-S (Mixes C and E); Buna-85 (A) is distinctly better, and Buna-N (F) is outstandingly good, being substantially unaffected by any of the liquids. Konrad[9], using nitrobenzene at 75° C, obtained a rather different order, Buna-S giving the most swelling, followed in decreasing order by Buna-85, Buna-N and Buna-115.

It is interesting to compare the behavior of Buna-N and natural rubber ebonites with that of soft vulcanizates made from Perbunan and natural rubber[7]. The results for the latter are as follows (no experiments were made with petroleum ether).

	Benzene	Gasoline	Carbon disulfide	Nitrobenzene
Swelling of Perbunan vulcanizate	182	21	63	255
Swelling of rubber vulcanizate	285	259	343	69
Ratio: Perbunan/rubber	0.64	0.08	0.18	3.7

With ebonite the ratio: Buna-N/rubber, for those liquids with a marked swelling action, is much smaller, namely, 0.007–0.008 for benzene, carbon disulfide, and nitrobenzene. The superiority in swelling resistance of a butadiene-

TABLE IV

SWELLING (PERCENTAGE BY VOLUME)

Liquid	Period of immersion (days)	A	B	C	D	E	F
Benzene at 25° C	1	0.2	7.6	0.5	0.2	0.4	0.0
	2	0.3	11.0	0.7	0.2	0.6	0.0
	4	0.4	17.0	1.1	0.4	0.8	0.1
	7	0.5	25.4	1.5	0.4	1.2	0.1
	14	0.8	41.0	2.2	0.4	1.6	0.0
	21	0.9	53.1	2.9	0.5	2.2	0.0
	28	0.9	56.6	3.6	0.5	2.9	0.1
	43	1.5	56.3	5.0	0.6	3.8	0.1
	70	2.0	...	7.3	1.3	6.3	0.4
	98	2.1	...	9.5	1.7	7.7	0.7
	126	2.3	...	11.0	1.6	9.0	0.7
	154	2.3	...	12.9	1.5	10.4	0.5
	182	2.0	...	14.0	1.1	11.0	0.3
Petroleum ether at 25° C	2	0.3	0.5	0.0	0.0	0.0	0.0
	4	0.3	0.8	0.2	0.0	0.1	0.0
	7	0.1	1.0	0.1	0.0	0.1	0.0
	14	0.1	1.4	0.2	0.0	0.0	0.0
	21	0.1	1.6	0.2	0.0	0.0	0.0
	28	0.1	2.1	0.2	0.1	0.1	0.0
	43	...	2.5	...	...	...	...
	57	0.4	3.2	0.2	0.3	0.3	0.0
Gasoline at 25° C	2	0.0	1.8	0.1	0.0	0.0	0.0
	4	0.0	2.6	0.1	−0.1	−0.2	−0.2
	7	−0.2	4.0	0.1	−0.1	−0.2	−0.1
	14	−0.1	6.3	0.2	0.0	−0.2	−0.1
	21	−0.2	8.0	0.3	0.0	−0.2	−0.1
	29	0.2	10.5	0.7	0.2	0.0	0.0
	43	0.1	12.5	0.8	0.1	0.0	0.0
	64	0.2	16.6	0.9	0.1	0.2	0.0
	98	...	21.6	...	...	...	...
	120	...	24.5	...	...	...	...
Transformer oil at 70° C	7	−0.3	−0.1	0.0	−0.1	−0.2	−0.8
	14	−0.2	0.1	0.1	0.0	0.0	−0.5
	21	−0.2	0.1	0.1	0.0	0.0	−0.5
	28	−0.2	0.1	0.0	0.0	0.0	−0.5
Carbon disulfide at 25° C	1	20.2	52.8	41.9	14.4	41.7	0.4
	2	33.3	57.0	46.0	23.4	52.5	0.6
	4	38.2	52.2	45.6	37.7	51.1	0.7
	7	38.7	56.3	47.5	38.3	52.1	0.9
	14	41.2	52.8	46.4	37.8	52.5	1.2
	21	39.7	59.0	45.5	37.7	50.3	1.3
	29	39.1	60.7	45.7	37.7	51.3	1.5
	56	...	...	...	...	...	2.3
	84	...	...	...	...	...	2.8
	126	...	...	...	...	...	3.3
	168	...	...	...	...	...	3.8
Nitrobenzene at 25° C	7	0.1	3.1	0.2	0.0	0.1	−0.1
	14	0.2	4.9	0.4	0.1	0.3	0.0
	21	0.2	6.0	0.4	0.1	0.3	0.0
	28	0.2	7.1	0.4	0.1	0.4	0.0
	42	0.3	8.9	0.6	0.2	0.6	0.1
	56	...	10.6	...	...	0.6	0.2
	77	...	13.1	...	...	...	...
	91	...	14.3	...	...	...	...

TABLE V

Liquid	Benzene	Petroleum ether	Gasoline	Transformer oil (a)	Carbon disulfide	Nitrobenzene
Period of immersion (days)	150	56	64	28	3	50
Mix A	2.3	0.4	0.2	−0.2	37	0.4
Mix B	56	3.2	16.6	0.1	54	9.8
Mix C	12.5	0.2	0.9	0.0	46	0.7
Mix D	1.5	0.3	0.1	0.0	32	0.2
Mix E	10.0	0.3	0.2	0.0	52	0.6
Mix F	0.5	0.0	0.0	−0.5	0.6	0.2
65:35 rubber-sulfur(b)	62	−0.1(c)	(d)	(e)	83(c)	27(f)

NOTES: (a) at 70° C. (b) Vulcanized for 5 hours at 155° C. (c) From Reference 8. (d) No data available. (e) Various samples gave values between −0.2 and −0.25. (f) Increases to about 65 ultimately[8].

acrylonitrile polymer thus appears to be much greater in an ebonite than in a soft vulcanizate.

The better resistance to swelling of Buna ebonites could arise from one or both of two factors: smaller maximum absorption and slower approach to the maximum, *i.e.*, longer swelling time. The latter may be an important factor, since it is known that in some cases an extremely long time is required to reach maximum absorption. In many of the present experiments it is not possible to estimate the two factors separately, because complete time-swelling curves were not obtained. In the few cases where the full curve is available the conventional swelling characteristics, namely, swelling maximum and periods of time required to reach ¼, ½, ¾, respectively, of the maximum (denoted by $t_{1/4}$, $t_{1/2}$, $t_{3/4}$), have been calculated and are given below; no reliable figures for increment could be obtained.

Liquid	Mix	Swelling maximum	$t_{1/4}$	$t_{1/2}$	$t_{3/4}$
Benzene	B	56	70 hrs.	195 hrs.	340 hrs.
Carbon disulfide	A	40	...	25 hrs.	40 hrs.
	B	54	...	...	<24 hrs.
	C	46	...	...	<24 hrs.
	D	28	15 hrs.	38 hrs.	63 hrs.
	E	52	...	...	22 hrs.

The swelling maxima are of the order of one-half the corresponding figures for natural rubber ebonites, and the swelling times are longer, especially with carbon disulfide, where $t_{3/4}$ for natural rubber ebonite is only about 5 hours[8]. This slower absorption can be ascribed, in part at least, to the higher state of vulcanization of the Buna ebonites (see paragraph 1 above), since it is known that the rate of absorption decreases rapidly as the combined sulfur is increased.

ELECTRICAL SURFACE DETERIORATION IN LIGHT

The Buna ebonites were tested in comparison with a 68:32 rubber-sulfur ebonite (H92A) vulcanized for 5 hours at 155° C. The tests were made by the method of the Research Association of British Rubber Manufacturers[10], using an improved exposure apparatus and mercury-vapor lamp. One exposure box contained Buna ebonites A–D with H92A for comparison, and another box Buna ebonites E and F, also with a specimen of H92A. The 11-hour vulcanizates of the Buna mixings were used. Throughout the experiments, air at 75 per cent relative humidity was circulated over the specimens.

Measurements of surface resistivity were made after several periods of exposure, and the logarithm of the resistivity plotted against the exposure period. The results in Table VI were read off from the smoothed curves.

TABLE VI

LOGARITHM OF SURFACE RESISTIVITY (OHMS)

Period of exposure (hours)	Box I					Box II		
	A	B	C	D	H92A	E	F	H92A
0	17.8	18.1	>19	18.1	17.9	18.0	17.1	17.5
3	17.2	17.6	17.5	17.4	17.7	18.2	16.4	16.4
6	16.7	16.5	16.3	16.6	17.5	16.6	15.1	15.8
9	15.8	14.3	14.0	14.7	16.2	14.9	13.6	15.3
12	14.1	13.1	12.6	13.6	15.3	14.1	13.0	14.7
18	12.5	12.4	12.0	12.6	13.9	13.0	12.3	13.5
24	11.5	11.7	11.4	11.7	12.6	12.1	11.7	12.6
30	10.7	11.1	10.8	10.8	11.7	11.2	11.1	11.9
40	10.4	10.6	10.2	10.4	11.0	10.0	10.2	11.0
50	10.2	10.3	10.0	10.2	10.8	9.7	9.9	10.6
60	10.0	10.2	9.8	10.0	10.6	9.5	9.8	10.3
Hours to 10^{14} ohms	12½	9½	9	10½	17½	12½	8	15½

All the Buna ebonites give good values of surface resistivity before exposure to light, and are similar to natural rubber ebonite. They all deteriorate more quickly when exposed to light, however, and judged by the number of hours required to bring the resistivity down to 10^{14} ohms, the deterioration of some of the Buna ebonites is almost twice as rapid as that of the natural rubber ebonite. With respect to light stability, therefore, Buna ebonites show no superiority.

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RUBBER RESINS: SOME PROPERTIES AND POSSIBILITIES OF USE *

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War conditions have not only stimulated the production of rubber from wild trees, shrubs, and plants, but many workers have been brave enough to attempt transplanting experiments and investigations of the rubber content in herbs and plants which have for years been considered of little importance.

Plantation rubber and a few forms of wild rubber contain very low percentages of resin, and no attempt is made for removal on an industrial scale. There is experimental evidence that this resin protects the raw rubber from the effects of air and light during the interval before it is made into useful objects. Some forms of wild rubber, however, contain as high as 80 per cent of resin, and the demand for the rubber hydrocarbon is such that these rubbers are deresinated, and the resin is sold as a byproduct.

Two examples of group are gutta-percha and balata, the hydrocarbons of which are desired for their thermoplastic properties; in other words they soften on heating and harden again on cooling, with slightly altered properties, and can be made to fit diverse forms. Today, while the synthetic rubber development is being pushed ahead rapidly, much effort is being made not only to stimulate increased production of wild rubber, but also to test all the likely looking plants, shrubs and trees which have ever been known to contain any rubber, of which there are about 260 known varieties.

It is likely that rubber resins may now be accumulating as a result of the above program, and to meet the needs of one who is considering the adoption of such resins or fuse in his products or to aid a producer or distributer in finding fields of use, the writer has gathered available information into one manuscript, and hopes that it will meet a need, because similar information is scattered widely through the most modern texts and journal articles.

Records show that, up to 1918, only guayule and jelutong (dead Borneo and pontianak) were subjected to extraction on a commercial scale, and when this was discontinued on resumption of normal imports from the plantations, deresinized gutta-percha and balata were slowly making progress. During and following the late World War, it was rumored about that pontianak resin was so plentiful that it was used as a binding agent in such inexpensive items as flexible asphalt joints, putties, and pipe-joining compounds.

HISTORY OF RUBBER RESINS

The percentage contents of resins in various grades of rubber and the properties of each were for a long time the subject of research by rubber scientists; in fact it was of interest in the middle of the last century and was progressing at the maximum rate around the turn of this century; one object was to establish standards, if possible, for the identification of wild rubber at the ports of entry.

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Although interest may have slackened in the past decade, much information is now available from which the use or field of use can be predicted. Some experimenters have even attempted to investigate the condition of the resin in the rubber, for example, whether it is present in an adsorbed form or intramolecularly placed; and although this question is still one of controversy, new and improved methods of extraction have been contributed to rubber technology. Measurements of optical activity, acid number, saponification number, and degree of unsaturation have shown that these resins are of complex chemical structure; methods of separating them into various fractions by changing the solvent and the temperature of extraction have led to the conclusion that even though there are variables in the method of drying and extracting, a rubber resin is defined as the acetone-soluble portion which is extracted under prescribed conditions.

RESIN CONTENTS OF VARIOUS RUBBER VARIETIES

The fact is well established that the resin contents of different forms of rubber depends on the method of coagulation, type and age of the tree, degree of rainfall and other factors; hence the figures in Table I cover the upper and lower limits, when they are available.

The high value of evaporated latex compared to the three plantation varieties just above it in the table adds more evidence to the generalized assumption

TABLE I

Type of Rubber	Resin content (percentage)
Plantation pale crepe	1.80– 3.00
Plantation sheet	2.50– 3.00
Plantation smoked crepe	2.50– 3.50
Evaporated latex	5.00– 6.00
Hard fine Para	3.00– 3.50
Ceara scraps	3.00– 5.00
Cameroon balls	7.00–10.00
Lagos lumps	10.00
Guayule	13.00–18.00
Jelutong	70.00–80.00
Oxidized rubber	60.50
Castilloa	18.90
Balata	37.18–48.97
Gutta-percha	37.67

that, in coagulating, a fraction of the resin is coagulated and removed with the rubber; the balance passes into the filtrate or serum. The value of 60.50 per cent for oxidized rubber is a variable and depends on the age and conditions. The value of 7.00–10.00 for Cameroon balls is higher than that of evaporated latex, but can be classed with it with respect to the method to removal from the latex, and further illustrates the variation with the source of the latex and the care given to it in preventing the entrance of foreign materials. The value of 13.00–18.00 for guayule and the desirable properties of the rubber hydrocarbon, which is present with the resin, might place it in a class of which extraction methods would be commercially profitable.

Table I is extended into Table II to show more properties of these resins, and there are some blank spaces after balata, gutta-percha, and jelutong resins because they depend on the source and will be presented more fully in later paragraphs. The physical forms of these resins differ, and all that have come to the writer's attention have been plastics with varying degrees of softness

except one, which had apparently been processed into an ester or had been compounded with common rosin. It was yellow, opaque, completely extracted with acetone, did not saponify, and its acid number was 121. An unscrupulous dealer was offering it to the public as a wax.

The above is an example of the incompleteness of the data available on rubber resins, but even though the blank spaces above might be filled with

TABLE II

Type of rubber	Some properties of nonsaponifiable (percentage)	Rubber resin melting point (° C)	Acid number	Nature (physical form)
Plantation pale crepe	15.00	...	135–136	
Plantation sheet	...	...	...	
Plantation smoked sheet	...	...	...	
Evaporated latex	...	...	...	
Hard fine Para	25.40	...	...	
Ceara scraps	...	...	172	
Cameroon balls	...	...	...	
Lagos lumps	...	...	...	
Guayule	78.20	...	240	Paste
Jelutong	83.20	82.00	...	
Hevea sheet	48.30	...	...	
Dyera crepe	77.80	...	...	
Oxidized rubber	2.40	...	...	
Castilloa	73.70	...	...	
Balata	...	...	...	Paste
Gutta-percha	...	...	...	
Congo	68.30	74.00	43	Paste
Borneo	...	92.50	...	

information from unpublished data, it would be a hollow victory, because we are interested here only in those resins which are extracted and are for sale to the public. They will be described more fully in later paragraphs. Ball rubber, guayule, Jelutong, balata, and gutta-percha may be the only ones available. Guayule resin adds sulfur at vulcanization temperatures and becomes hard, brittle, and opaque. Jelutong does not add, sulfur.

Another example of how the Balata resin differs with the source of the material is that of Iquitos, which has a hard brittle resin after extraction and removal of the solvent; whereas Surinam leaves an oily liquid with the same method of extraction. Gutta-percha resin has been coming into commerce in three forms, and the differences can be attributed to the amount of residual solvent in each. They are (1) hard, transparent, and dark red in heavy layers; (2) white and waxy, but changing slowly with age; (3) viscous oils. There are some reports that it is now being rolled out into sheets and sold as a special plasticizer.

In view of the fact that oxidized jelutong (pontianak) has been readily available for sale to the public, some properties of three samples are listed in Table III.

TABLE III

Sample number	Acid number	Saponification number	Iodine number	Acetone-soluble (percentage)	Melting point (° C)
1	3.50	70.00	43.20	99.50	74.00
2	4.10	48.10	44.00	99.30	82.00
3	...	28.10	...	...	92.50

Judging by the percentage content of the portion soluble in acetone, it is apparent that the rubber hydrocarbon is almost completely converted to resin; a condition which occurs with other forms and types rubber. The gradual rise in melting point suggests that Sample No. 3 still contains some unoxidized rubber hydrocarbon.

Jelutong usually comes into the market in the form of cakes, containing about 70 per cent of moisture and preservatives to prevent the growth of moulds, and only in this form will certain manufacturers purchase it; but the dry oxidized form has been for sale to gum and rosin users under various misleading names like Elastica, etc. It has not been possible to determine the history of drying and oxidation.

Owing to the fact that the resin of jelutong or the oxidized form described earlier is not attacked by alkalies, its use was suggested for coatings on lime rich cements and concrete, also to substitute for a portion of the rosin (colophony) in paper sizes. These alkali-resistant coatings may have been replaced with synthetic resins of the cumar type, but the commercial possibilities of them led Ellis[1] to investigate their behavior on heating in open kettles and kettles equipped with air of water coolers for return of the distillates or portions of them to the kettle. He also investigated the behavior in commercial paint vehicles. His data are presented in Table IV.

TABLE IV

Sample number	Heating (hours)	Temp. (° C)	Loss (%)	Fusion point (° C)	Physical condition
1			0.00	126	White powder
2	12	204	3.10	77	Hard and clear
3	10	232	5.90	78	Hard and clear
4	9	264	13.10	78	Hard and clear
5	1	316		77	Hard and clear
6	3.5	343	50.00		Hard and clear
7	5	343	10.00	65	Hard and clear
8	4	343	16.00		Plastic
9	6	343	18.00		Plastic (flowed)
10		Destructive Distillation			Oil

These tests were made with jelutong from Sarawak, Dutch Borneo, Sumatra, and the Malayan peninsula. At the port of entry the cakes had the following approximate composition: 10 per cent rubber hydrocarbon, 20 per cent resin, and 70 per cent water. Included in the solid contents are proteins and other naturally occurring plant compounds, which are not recorded and are altered or destroyed on heating.

The iodine number of the crude white powder before heating was 36, that of Sample No. 9 was 62, and that of the oil in Sample No. 10 was 93. This is indicative of very complicated changes, which cannot be explained with meager data.

Sample No. 1 was the acetone-extracted resin of commerce, which is in the form of white powdery, friable lumps; Samples No. 2, 3, 4, 5, and 6 were heated in open kettles, from which was a free escape of vapors; Sample No. 7 was heated under a water-cooled reflux condenser, and Samples No. 8 and 9 were heated under an air condenser of the reflux type, which allowed the vapors of acetic acid and other highly volatile compounds to escape, but the oils were returned to the metl. Samples No. 1–5, even though they had been heated at different temperatures over different time intervals, showed an approach to a constant fusion point of 77 to 78° C up to a temperature of heating of 316° C.

TABLE V

Solvent used	Resin No. Table 4	Quantities (grams) of solvent and resin mixed: Solvent	Quantities (grams) of solvent and resin mixed: Resin	Grams solid resin dissolved
Benzene	1	50	50	19.00
Benzene	2	50	50	29.50
Benzene	5	50	50	28.00
Benzene	2	60	40	20.00
Benzene	3	60	40	19.60
Benzene	4	60	40	19.20
Benzene	4	66	34	13.94
Benzene	4	71	29	11.04
Benzine, light	2	60	40	17.20
Benzine, light	3	60	40	17.60
Benzine, light	2	66	34	13.94
Benzine, light	3	66	34	13.60
Benzine, light	4	66	34	13.60
Benzine, light	5	66	34	13.26
Benzine, light	4	71	29	10.73

The sharp drop of fusion point after heating for one hour at 316° C suggests that longer periods of heating at lower temperatures are uneconomical, even though the same fusion point of the resulting melt is reached at 204° C after heating for 12 hours with a loss of 3.10 per cent.

These melts or fused resins were immersed in commercial solvents and, after standing for extended periods, the clear supernatant varnishes were decanted and analyzed. In view of the fact that mixed solvents showed no particular advantage over pure ones, the results with them are omitted here, and only those for commercial benzene and light benzine are presented. They appear in Table V.

TABLE VI

SOLUBILITY OF GUTTA-PERCHA RESIN

Solvent	50 Gutta-percha resin 50 Solvent: 20° C	50 Gutta-percha resin 50 Solvent: 100° C	25 Gutta-percha resin 75 Solvent: 20° C	25 Gutta-percha resin 75 Solvent: 100° C
Benzene	t. l.	l.	l.	
Toluene	t. l.	l.	l.	
Xylene	t. l.	l.	l.	
Petroleum ether	f. u.	f. u.	f. u.	f. u.
Tetralin	t. l.	l.	t. l.	l.
Methanol	w. l.	w. l.	w. l.	w. l.
Ethanol	t. l.	l.	t. l.	l.
Butanol	t. l.	l.	t. l.	l.
Amyl alcohol	t. l.	l.	t. l.	l.
Hexalin	w. l.	l.	w. l.	l.
Methylhexalin	w. l.	l.	w. l.	l.
Ether	l.			
Acetone	l.			
Methylethyl ketone	l.			
Diacetone alcohol	t. l.	l.	t. l.	l.
Ethylglycol	t. l.	l.	l.	
Methyl acetate	l.			
Ethyl acetate	l.			
Butyl acetate	t. l.	l.	t. l.	l.
Amyl acetate	t. l.	l.	l.	
Hexalin acetate	t. l.	l. x.	f. u.	l. x.
Tricresyl phosphate	f. u.	l. x.	f. u.	l. x.
Castor oil	f. u.	x at 150° C		x at 150° C

t. l.—partly soluble
l.—easily soluble
f. u.—almost insoluble
x.—solidified on cooling
w. l.—slightly soluble

The results with turpentine and solvent naphtha, also the physical condition of the film on glass slides are available, but omitted here. Samples No. 2 and 5, histories of which are in Table IV, show the highest degree of solubility in benzene. Comparison of the figures in the fifth column for those of benzene and light benzine show that benzene is the better solvent, and that the resin must have been fused for a time interval to attain the maximum solubility of 29.50 in 100 grams of varnish because Sample No. 1, which had received no heat treatment, but was only melted and when thinned with benzene, showed a solubility figure of 19 compared to 29.50 for one which had undergone a loss of 3.10 per cent during heating at 204° C for 12 hours.

The information available on the solubility of gutta-percha and balata resins in various solvents is somewhat indefinite; and instead of figures for the amount of solid resin found in a definite volume or weight of varnish (clear) after settling, only approximations like slightly soluble and completely soluble are available.

The data of Merz[2] are presented in Table VI. Although no solubility figures are available, the approximate behavior at two temperatures and two concentrations in twenty-five solvents may be of aid in choosing a solvent for this resin in meeting a practical need.

TABLE VII

SOLUBILITY OF BALATA RESIN

	50 Balata resin 50 Solvent		25 Balata resin 75 Solvent	
	20° C	100° C	20° C	100° C
Benzene	t. l.	l.	l.	
Toluene	t. l.	l.	l.	
Xylene				
Petroleum ether	t. l.	t. l.	l.	
Tetralin	t. l.	l.	l.	
Methanol	f. u.	t. l.	f. u.	t. l.
Ethanol	f. u.	t. l.	f. u.	t. l.
Butanol	f. u.	t. l.	f. u.	t. l.
Amyl alcohol	f. u.	t. l.	f. u.	t. l.
Hexalin	f. u.	l.	f. u.	l.
Methylhexalin	f. u.	l.	f. u.	l.
Ether	l.			
Acetone	f. u.	f. u.	f. u.	f. u.
Methylethyl ketone	t. l.	t. l.	t. l.	t. l.
Diacetone alcohol	f. u.	f. u.	f. u.	f. u.
Ethylglycol	f. u.	t. l.	f. u.	t. l.
Methyl acetate	t. l.	t. l.	t. l.	t. l.
Ethyl acetate	t. l.	t. l.	t. l.	t. l.
Butyl acetate	t. l.	t. l.	t. l.	t. l.
Amyl acetate	t. l.	t. l.	t. l.	t. l.
Hexalin acetate	t. l.	l.	l.	

l.—easily soluble
t. l.—partly soluble
f. u.—insoluble
x.—solidified on cooling
w. l.—slightly soluble

In benzene, toluene, and xylene, the gutta-percha resin is soluble at room temperature up to and around 25 per cent resin, but at 50 per cent resin and the same temperature the solution is saturated, and undissolved resin settles to the bottom. In like manner the balance of the table can be interpreted.

The information on the solubility of balata resin is of the same approximate nature as that of gutta-percha, and is in Table VII.

With benzene, toluene, and xylene, this resin behaves somewhat similarly to gutta-percha resin. Beyond this statement the table only points the way to one who wishes to use one of these resins, and is restricted by the solvent and conditions to be met, beyond that one must experiment.

The methods of extracting rubber resins on a commercial scale with volatile solvents have been described in texts and former journal articles. What is more, they have been the subject of certain patents; hence they need not be described again here.

SUMMARY AND CONCLUSIONS

However, their present uses and possible future uses deserve consideration. Their tendency to thicken in certain solvents has been applied to use in imparting false body (thickening) to certain varnishes. In such cases it is likely that the rubber resin is modified to reduce tackiness before compounding it into quick-drying spirit varnishes. As plasticizers for brittle resins and asphalts they afford a very inexpensive raw material. But, again, experiments must be performed to see if the rubber resin is compatible with the natural or synthetic one, as there is little information as to whether plasticizers form solid solutions or only mechanical mixtures with the resins after heating and mixing.

In one case a large shoe manufacturer purchased many tons of gutta-percha resin for impregnation of threads used in sewing on soles; the object was to prevent the entrance of moisture into the shoe and to supply a flexible adhesive. Electric friction tape, which must have an eversoft tacky surface, is coated with a compound of a bitumen, regenerated rubber, and a gutta resin, and is similar in composition to readily appliable insulation pastes, which are used on underground electric cables.

The use in ever-soft adhesives and in flypaper are only two of the minor ones. The application of these resins to textiles in the form of emulsions shows large possibilities, as they can be emulsified with ammonium oleate or linoleate and, on drying, leave behind films of rubber resin and the fat acid of the emulsifier. A hardened balata resin has been used in linoleum cement. The soft resin or even the oily one can be hardened by heating for four hours at 80° C, after adding 1 per cent of manganese resinate or 0.5 per cent of calcium carbonate. Treatment of the same resin with sulfur chloride results in a viscous resin which, when warm, can be pulled out into ropes like taffy candy and, when cold, is still viscous.

In closing, the writer wishes to state that, even if a reader may fail to find here the exact information he desires about a certain rubber resin, let it be hoped that what information he does find will save many hours of fruitless toil.

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DETERMINATION OF TOTAL AND COMBINED SULFUR IN BUTYL RUBBER *

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In the course of certain polymer studies in this laboratory, it became necessary to determine the amounts of total and combined sulfur in Butyl rubber vulcanizates. No previously published method of analysis was available for this class of synthetic rubbers. It seemed worthwhile to disclose the analytical procedure described below, because it may have a wider possible field of application than that for which it was originally developed. Some of the problems that may be studied with the aid of this method are rate of vulcanization, behavior of various accelerators, sulfur blooming, and factory control.

The numerous methods that have been devised for determining total and combined sulfur in natural-rubber compositions are adequately described, or referred to, elsewhere[1]. A commonly used procedure consists in analyzing the composition for total sulfur by oxidation of the sulfur to sulfate with such reagents as nitric or perchloric acid, followed by determination of the sulfate in the usual manner by precipitation as barium sulfate. Free sulfur is considered to be completely extractable from the vulcanizate, exhaustive treatment with acetone being employed almost universally for this purpose. The sulfur in the acetone extract is commonly determined as barium sulfate, after oxidation with a nitric acid-bromine mixture. The difference between the total and extractable sulfur values is regarded as chemically combined sulfur. No discussion need be given here of the familiar complications sometimes introduced by the presence of inorganic sulfides and sulfates, some accelerators, and various compounding ingredients that contain sulfur.

Early in this work it was found that the procedure described for natural rubber could not be applied successfully to Butyl rubber. The principal reasons for the difference in behavior appeared to be twofold: Butyl rubber compositions are less permeable to acetone, and their stability toward oxidizing agents exceeds greatly that of natural rubber. Neither the vulcanizates nor the acetone-extractable materials (which contain small percentages of low-molecular components of the polymer) could be readily oxidized, even after protracted treatment with hot oxidizing solutions. Furthermore, acetone proved to be a very poor agent for removing extractable sulfur under the conditions employed in this work. It was found, however, that the latter could be completely extracted within 8 hours by means of methylethyl ketone. This solvent appears to swell Butyl vulcanizates sufficiently well to hasten sulfur diffusion very markedly, and its use does not result in the excessive oxidative depolymerization reported by Cheyney[2] for natural rubber. While it is conceivable that the behavior of acetone might be satisfactory in the

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method of hot extraction recommended for natural rubber by the A.S.T.M. instead of standard Soxhlet extraction as used in this work, it is believed that methylethyl ketone would still prove to be a superior extraction agent, although further experiments would be necessary to verify this point. It was found also that the total sulfur in the original vulcanizate, as well as the combined sulfur remaining after extraction with the ketone, could be readily determined as barium sulfate by burning the sample in a Braun-Shell sulfur apparatus (Braun Corporation, Los Angeles, California), the sulfur oxides formed then being converted to sulfate by absorption in alkaline sodium hypobromite solution. Extractable sulfur is, of course, given by the difference between the total and the combined sulfur values.

In view of the ease with which these determinations can be carried out, the excellent results obtained, and the low cost of methylethyl ketone, it was considered unnecessary to study the applicability of other ketones, although the use of higher ketones might enable one to reduce still further the time required for complete extraction.

APPARATUS

The air-purifying train is similar to that described by Zahn[3], and is composed of an air filter, furnace, cooler, gas-washing bottles, spray trap, manifold, and flowmeter. The air filter is inserted directly in the compressed air line. The air passes from this device into an electrically heated, stainless steel tube,

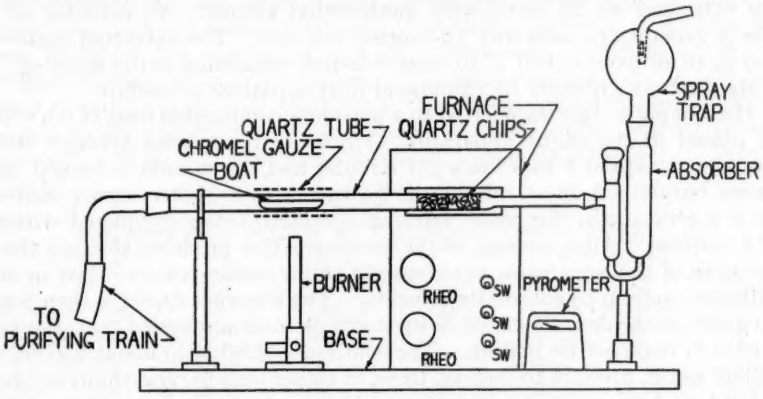

FIG. 1.—Diagram of Braun-Shell sulfur apparatus

partly filled with quartz chips and maintained at approximately 800° C. This leads to a water-jacketed copper-coil cooling tube, from which the gas issues into a washing bottle containing 2 per cent alkaline sodium hypobromite solution, followed by a similar bottle containing 2 per cent sodium hydroxide. The purified gas then passes through a spray trap into a constant-pressure manifold, each outlet of which is equipped with a calibrated flowmeter. Constant pressure is maintained on the manifold by means of a mercury-water seal equivalent to 48 mm. of mercury. The purified air then passes directly into the combustion tubes of a Braun-Shell sulfur apparatus (Figure 1). The air-purifying train described above can doubtless be modified and perhaps simplified without any serious sacrifice in efficiency, and thereby be adapted to more modest available equipment.

The Soxhlet extraction apparatus consists of the standard, all-glass type, of a size sufficiently large to hold a 34 × 100 mm. Alundum thimble (RA98, coarse; A. H. Thomas Co.).

REAGENTS AND SOLUTIONS

The acetone and methylethyl ketone are of commercial grade, dried with, and distilled from, anhydrous potassium carbonate prior to use. The alkaline sodium hypobromite solution is prepared by dissolving 112 grams of bromine and an equal weight of sodium hydroxide in 2600 cc. of distilled water, and the resulting stock solution is diluted for use with 3 volumes of distilled water. Except for the ketones, all chemicals used in this work are of reagent grade, and all solutions are prepared with distilled water.

PROCEDURE

About 0.5 gram of the rubber sample is carefully weighed and cut into 2- to 3-mm. cubes. In this range of subdivision the rate of extraction of the material is not critical. The comminuted sample is placed in the thimble of the Soxhlet apparatus and extracted at a siphoning rate of approximately 5 minutes. When unvulcanized samples are used, the cubes cohere after a short period of extraction. This is successfully prevented by mixing the material with a small amount of 20- to 30-mesh Ottawa sand that has previously been extracted for 24 hours with methylethyl ketone. No cohesion of particles is experienced with any vulcanized samples. The extracted material is dried in an air oven at 100° C to remove ketone remaining in the sample. This drying step can probably be eliminated from a routine procedure.

The sample is then transferred to a porcelain combustion boat (Coors No. 2) and placed in the sulfur apparatus. Purified air is passed through the apparatus at a rate of 2 to 3 liters per minute, and the sample is burned with a Bunsen burner. A short subsequent heating with a Méker burner suffices to give a colorless ash, the entire burning operation being completed within 10 to 15 minutes. After passage of the decomposition products through the furnace zone of the apparatus, the resulting sulfur oxides are absorbed in 50 cc. of alkaline sodium hypobromite solution. The absorber liquid is then washed into a 400-cc. beaker, 25 cc. of *N* hydrochloric acid are added, and the excess bromine is removed by boiling. The solution is diluted to about 250 cc. with distilled water, brought to boiling, 10 cc. of 10 per cent barium chloride solution is added, and the precipitated barium sulfate is digested overnight on a steam bath. The precipitate is filtered, washed, dried, and weighed in the customary manner. For determining of total sulfur, the same procedure is employed, the extraction step being omitted.

With samples containing very small percentages of sulfur, or with unvulcanized compositions from which almost all of the sulfur has been removed by extraction, the barium sulfate is determined turbidimetrically by the method described by Zahn[3].

EXPERIMENTAL RESULTS

A blank run was made for the purpose of determining the sulfur contributed by the reagents and apparatus. The amount of purified air passed through the apparatus was approximately equal to that used in the subsequent rubber analyses. A sulfur blank of 0.005 per cent was obtained.

Two samples of Butyl rubber were used in preparing the compositions discussed in this paper. In Table I are recorded some characteristic properties of these two materials. Blank determinations carried out with samples of these two polymers gave sulfur values of 0.010 per cent for Butyl 1 and 0.008 per cent for Butyl 2, corrected for the reagent blank.

TABLE I

PROPERTIES OF CRUDE BUTYL RUBBERS

Polymer	Intrinsic viscosity in diisobutylene at 20° C[4]	Molecular weight (viscosity average[4])	Unsaturation mole-percentage[5]
Butyl 1	1.25	370,000	0.51
Butyl 2	1.28	385,000	0.71

To determine the relative efficiencies of extraction by acetone and methylethyl ketone, a set of experiments was carried out with a milled, unvulcanized mixture composed of Butyl 1 100 parts, carbon black 7.0 parts, and sulfur 1.5 parts. Assuming no losses of moisture or of any of the components during mill mixing, the calculated sulfur content of the mixture was 1.39 per cent. Analysis by the method under discussion gave values of 1.40, 1.42, and 1.41. The comparative behavior of the two solvents may be judged by the data given in Table II; acetone is not capable of removing sulfur completely within 72 hours, whereas methylethyl ketone gives constant values within 8 hours. The small percentage of sulfur remaining in the sample after exhaustive extraction with the latter solvent is believed to be chemically combined as the result of milling, although the possibility of some combination occurring during the extraction process must be recognized. Evidence for this view is presented below, and independent data supporting this conclusion have been obtained[6] in studies of the viscosities of similar milled mixtures. The superior swelling characteristics of the higher ketone are reflected in the data in Table II showing

TABLE II

EXTRACTION OF SULFUR FROM AN UNVULCANIZED MIXTURE

Time of extraction (hours)	Total S (%)	Acetone			Methylethyl ketone		
		S extracted (%)	S remaining in sample (%)	Total material extracted (%)	S extracted (%)	S remaining in sample (%)	Total material extracted (%)
5	1.41	0.69	0.72	1.4	1.36	0.05	2.9
8	1.41	1.00	0.41	1.4	1.39	0.02	3.0
16	1.41	1.16	0.25	2.1	1.39	0.02	3.2
30	1.41	1.23	0.18	2.1	1.39	0.02	3.4
50	1.41	1.29	0.12	2.1	1.39	0.02	3.2
72	1.41	1.37	0.04	2.5	1.38	0.03	3.8

the total amount of material extracted, these values with methylethyl ketone being somewhat larger than the corresponding values with acetone. No significant amount of degradation occurred during extraction, the total amount of extracted material showing only a slight upward trend with extraction time.

Analytical data of a corresponding nature are presented in Table III for a routine mixture based on the recipe Butyl 1 100 parts, zinc oxide 2.0 parts, carbon black 7.0 parts, sulfur 1.5 parts, and tetramethylthiuram disulfide 1.0 part: vulcanized for 60 minutes at 152° C. The total sulfur values for this composition were found to be 1.71, 1.69, 1.70 per cent. [The calculated sulfur content, 1.82, is probably incorrect because of errors in compounding or losses

during milling.] Table III shows that the extractable sulfur in the vulcanizate was not entirely removed after 72 hours of acetone extraction; on the other hand, constant values were again obtained within 8 hours with methylethyl ketone. The ash analyses show that roughly 0.01 per cent of sulfur remained in the ash. It will be seen from Table VI that approximately the same per-

TABLE III

EXTRACTION OF SULFUR FROM A VULCANIZED MIXTURE

Time of extraction (hours)	Total S (%)	Acetone				Methylethyl ketone			
		S extracted (%)	S remaining in sample (%)	S in ash (%)	Material extracted (%)	S extracted (%)	S remaining in sample (%)	S in ash (%)	Material extracted (%)
5	1.70	0.76	0.94	0.012	1.1	1.10	0.60	0.014	2.2
8	1.70	0.81	0.89	0.008	1.7	1.16	0.54	0.010	3.0
16	1.70	0.96	0.74	0.014	1.8	1.15	0.55	0.014	3.2
72	1.70	1.11	0.59	0.016	2.4	1.16	0.54	0.014	3.4

centage of sulfur was found in the ash of a composition containing 5.0 parts of zinc oxide.

To determine whether certain common accelerators are completely extracted under the above conditions, experiments were carried out with various unvulcanized mixtures, the compositions of which are given in Table IV.

TABLE IV

EXTRACTABILITY OF SULFUR AND ACCELERATORS FROM UNVULCANIZED MIXTURES WITH METHYLETHYL KETONE

Composition	Time of extraction (hours)	Sulfur remaining in sample	
		Butyl 1 (%)	Butyl 2 (%)
Butyl 100 Sulfur 3	8	0.05	0.06
	16	0.05	0.06
Butyl 100 Tetramethylthiuram disulfide 1	8	0.03	0.02
	16	0.03	0.02
Butyl 100 Mercaptobenzothiazole 1	8	0.03	0.03
	16	0.03	0.02
Butyl 100 Carbon black 50 Sulfur 1.5	8	0.05	0.05
	16	0.05	0.05
Butyl 100 Carbon black 50 Tetramethylthiuram disulfide 1	8	0.06	0.07
	16	0.07	0.07
Butyl 100 Carbon black 50 Mercaptobenzothiazole 1	8	0.06	0.07
	16	0.06	0.07

Parallel results are recorded for mixtures that had been prepared with the two polymers described in Table I. Table IV shows that extraction for 8 hours with methylethyl ketone is sufficient to remove virtually all of the sulfur, tetramethylthiuram disulfide, and mercaptobenzothiazole present in the compositions; furthermore, the presence of 50 parts of carbon black does not cause interference. The small percentages of residual sulfur shown in Table IV may be attributed to chemical combination during the milling procedure. The values for the mixtures containing the accelerators are observed to be somewhat higher when carbon black is present. This is readily explained by the fact that, on milling, the batch temperature is increased by the presence of the

carbon black, the chemical combination of sulfur from the accelerator thereby being enhanced.

The variation of combined sulfur with time of vulcanization is demonstrated by the data of Table V for several samples containing the two Butyl polymers of Table I. These compositions were prepared mainly for the purpose

TABLE V

DEPENDENCE OF COMBINED SULFUR ON TIME OF CURE FOR BUTYL VULCANIZATES

(Methylethyl ketone extractions)

Composition		Time of cure at 152° C (min.)	Time of extraction (hours)	Sulfur remaining in sample	
				Butyl 1 (%)	Butyl 2 (%)
I					
		0	8	Sample lost	0.07
Butyl	100	0	16	0.05	0.03
Zinc oxide	2	30	8	0.27	0.52
Sulfur	1.5	30	16	0.22	0.50
Tetramethylthiuram disulfide	1	60	8	0.38	0.71
		60	16	0.34	0.67
II					
Butyl	100	0	8	0.14	0.17
Zinc oxide	5	0	16	0.14	0.14
Sulfur	1.5	40	8	0.33	0.35
Stearic acid	3	40	16	0.32	0.35
Tetramethylthiuram disulfide	1	60	8	0.49	0.63
Carbon black	50	60	16	0.50	0.61
III					
Butyl	100	0	8	0.14	0.16
Zinc oxide	5	0	16	0.14	0.16
Sulfur	3	40	8	0.32	0.30
Stearic acid	3	40	16	0.35	0.30
Tetramethylthiuram disulfide	1	60	8	0.52	0.63
Carbon black	50	60	16	0.54	0.63

of securing analytical data for a few more or less representative mixtures, and are therefore not to be construed as indicative of the best known compounding formulas. The values of combined sulfur given in Table V are probably somewhat higher than would be found normally, since the samples were unfortunately allowed to remain in the laboratory for about 3 months before being extracted and analyzed. The data of Table V nevertheless prove that 8 hours of extraction with methylethyl ketone is ample for the removal of extractable sulfur from the compositions listed. The results furthermore serve to show that, as might be expected, the percentage of combined sulfur increases with time of cure; and for a given time of cure, it tends to be greater for the polymer containing the greater proportion of chemical unsaturation.

TABLE VI

ASH ANALYSIS DATA FOR SEVERAL EXTRACTED VULCANIZATES

Composition	Time of cure at 152° C (min.)	Time of extraction (hours)	S in ash (%)
I (Butyl 1)	60	8	0.012
	60	16	0.014
II (Butyl 2)	60	8	0.012
	60	16	0.013

To learn how much sulfur remained in the ash of the extracted vulcanizates of Table V, the extracted portions of composition I (prepared with Butyl 1) and of composition II (prepared with Butyl 2) were washed in the sulfur apparatus in the regular manner, and the sulfur contents of the residual ash determined. The results (Table VI) show that the amount of sulfur retained by the ash is about 0.01 per cent, which is practically negligible except in analyses requiring the greatest possible accuracy.

SUMMARY

Methylethyl ketone has been shown to be a much more effective solvent than acetone for the removal of extractable sulfur and certain accelerators from Butyl rubber vulcanizates in a standard Soxhlet extraction. The use of this extraction agent, together with combustion of the original and extracted samples in the Braun-Shell sulfur apparatus, provides a satisfactory procedure for determining the amounts of total and combined sulfur in Butyl compositions.

ACKNOWLEDGMENTS

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A NEW EXTRUSION PLASTOMETER *

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INTRODUCTION

Early studies of the processing characteristics of synthetic rubber (GR-S) indicated that it would be desirable to have a laboratory test to determine whether satisfactory tread slabs could be produced from a given batch of tread stock by extrusion through a plate die. In the factory, the material is extruded as a continuous slab, flat on one side and shaped on the other. The extruding material is put under tension and carried away by a moving belt. Since the central portion of the slab, which will eventually become the tire tread, is thicker than the adjoining sidewall portions, it is extruded at a greater rate. Therefore, tensile stresses are set up in the sidewalls after the stock leaves the die. The material either flows to relieve these stresses or it tears.

Preliminary work indicated that common methods[1] of measuring plasticity were not adequate to measure or predict the tendency of certain stocks to tear in the sidewalls. Therefore, it was decided to develop a test which should reproduce the essential features of factory extrusion in miniature and under close control. This was accomplished in a new extrusion plastometer by the use of special dies and of a device to apply tension to the extruding sample.

THE INSTRUMENT

The instrument consists essentially of an extrusion chamber, a die, a device for applying tension to the extruding sample, an air cylinder and piston, an air-pressure control system, a temperature control system, and a timing device. The details of the extrusion chamber are shown diagrammatically in Figure 1. The die rests on a ledge at the top of the chamber and is held in place by a lock ring. Above the die are two rollers through which the extruding sample passes. By means of a system of pulleys and weights, not shown in the diagram, a constant torque is applied to one roller. Another set of weights furnishes the force compressing the sample between the rollers. Thus the sample is extruded under constant tension. Constant temperature is maintained by circulating hot oil. Provision is made for the insertion of a needle thermocouple into the center of the sample at three places. A section of the lower part of the cylinder is cut out and hinged, forming a door which can be opened to clean out the cylinder. The air pressure applied to the piston is measured by a pressure gauge, and the time required for the piston to move a certain distance during the extrusion is measured by an electric timer. A diagram of the dumbbell die used is included in Figure 1.

The extrusion chamber is 1.5 inches in diameter and 4.5 inches long from the top of the door to the die. The sample is cut out in the form of disks 1.25 inches in diameter and 0.375 inch or less thick. For ease of handling, the disks are placed on a straight wire. This technique allows a sample weighing

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0.2 pound to be heated to 212° F in 15 minutes in an oven and to be transferred quickly to the extrusion chamber.

Factory extrusion conditions are simulated by a dumbbell die, consisting of two holes connected by a narrow slot. The material extrudes more rapidly through the large holes than through the narrow slot, with the result that tensile stresses are set up in the web. The material of the web must either

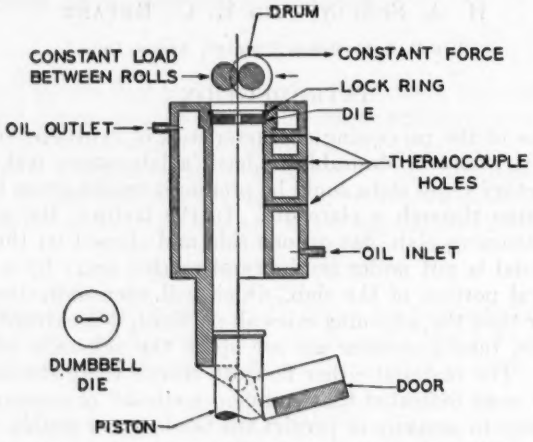

FIG. 1.—Diagrammatic sketch of the extrusion chamber and a dumbbell die.

flow or tear to relieve these stresses. The ability of a die to tear a given stock depends primarily on the relation between the cylinder diameter and the slot width, the latter being the more critical dimension. Table I gives the dimensions of some of the dies which have been used. Dies *A* and *D* are not dumbbell dies, and are used where information only on rate of extrusion is desired. Extrusion plastometers have been found by other workers[2] to be valuable in the measurement of the plastic properties of unvulcanized rubber compounds at high rates of shear. The plasticity is given by the rate of flow of the material

TABLE I

DIMENSIONS OF DIES

Die No.	Description	Die thickness (inch)	Cylinder diameter (inch)	Slot	
				Length (inch)	Width (inch)
A	Circular	0.250	0.205	—	—
D	Circular	0.240	0.104	—	—
F	Dumbbell	0.250	0.150	0.700	0.030
H-3	Dumbbell	0.125	0.150	0.600	0.030
H-4	Dumbbell	0.124	0.151	0.592	0.037

through a given die under given conditions. Although the instrument was designed primarily to indicate tearing by means of the dumbbell die, it can also measure extrusion rates. Successive measurements of the extrusion rate of a given stock give results which are as consistent as those obtained with the commonly used control instruments. Within the limits of experimental accuracy and in the range of rates studied, from 0.01 to 0.100 cu. in. per second, the extrusion rate varies as a power, usually four or less, of the pressure. Temperature has a comparatively small effect on extrusion rate.

FIG. 2.—Photographs of extruded samples, showing GR-S tread stocks from plasticized crude and one GR-I tread stock.

TYPICAL RESULTS

Effect of Plastication

In a factory processing test, several charges of GR-S were blended in a Banbury internal mixer, equal amounts of the blend were given from one to five passes through a Gordon plasticator, and tread batches were mixed from each lot. Samples of each lot of the crude and of the final batches were extruded in the laboratory. Figure 2 is a photograph of extruded samples of some of the tread batches. The appearance of the extruded samples of the final batches improved with plastication of the crude up to the third pass, but little further improvement is noted for the batches mixed from the crude plasticized four or five times. These laboratory results coincided with the factory tubing trials, even in the case of the batch, mixed from the one-pass crude, which did not seem to fit into the series. Another batch which was prepared from the same crude extruded well both in the laboratory and in the factory.

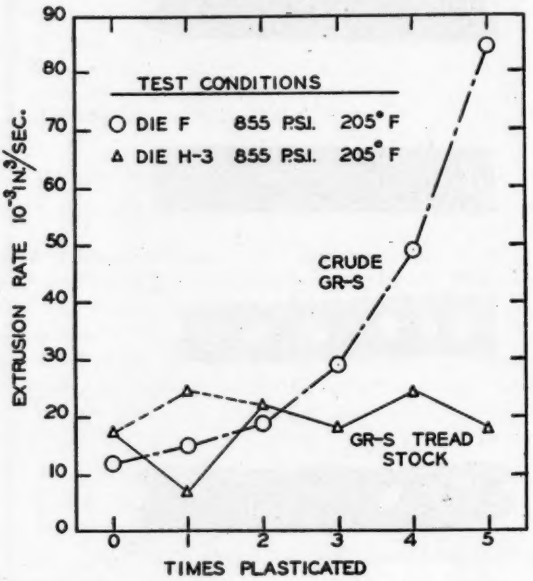

Fig. 3.—Effect of plasticization of crude synthetic rubber (GR-S) on the extrusion rates of the crude and of tread batches mixed from the crude.

A sample of butyl rubber (GR-I) is included in Figure 2 for comparison. It tubes very well in the factory, as would be expected from the appearance of the sample shown here.

Figure 3 shows how the plasticization of the crude affects the extrusion rates of the crude and of the final tread stocks. The crude becomes softer with each succeeding pass through the Gordon plasticator, but the tread stocks mixed from these crudes do not follow the same tendency. This effect was found also for stocks mixed from crudes which had been masticated for different times in a laboratory internal mixer. The tendency of a stock to tear does not necessarily correlate with the extrusion rate of the final batch or of the crude.

FIG. 4.—The effect of milling a GR-S tread stock that had aged 108 days at room temperature.

Effect of Storage and Milling

As a GR-S tread stock ages, it becomes tougher, and it tears more on extrusion. After a stock has been stored for some weeks it will extrude to give a rough, torn, sample, even though it extruded very well when it was freshly mixed. This aging effect proceeds at a greater rate at higher temperatures, and it occurs even in stocks without sulfur and accelerator.

If an aged stock is milled, its extrusion properties improve very noticeably. To study this effect, samples weighing 0.9 pound were cut from a sheet of tread stock which had been stored 108 days at room temperature. The samples were milled different amounts on a 6 × 12 inch mill and then extruded in the laboratory. A photograph of the results is given in Figure 4.

Factory mixed tread batches are subjected to a warm-up milling just before extrusion. The effect of storage and of subsequent milling was checked for seventeen GR-S tread stocks, and it was found that the usual factory warm-up milling brought all the stocks back to their original extrusion condition, even though some had been in storage for 15 days.

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DETERMINATION OF BRITTLE POINT OF RUBBER MATERIALS IN COLD AIR *

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The increasing demand for rubber and rubberlike materials that can withstand low temperatures in service necessitates suitable methods for evaluating their properties at subzero temperatures. Several investigators have selected brittle point or critical temperature of fracture as a criterion for evaluating the usefulness of a rubber material at low temperatures. Selker, Winspear, and Kemp[1] devised an immersion bath type of apparatus for determining the brittle points of rubber compositions on freezing. Recommendations for modification in the design of the equipment were proposed by Morris, James, and Werkenthin[2]. Data obtained in both investigations indicate that there is a definite temperature at which the material under test fractures when bent rapidly through 90°.

However, immersion bath tests have the disadvantage that the specimens are subject to extraction and (or) swelling by the cooling liquid. Therefore, it appears desirable to develop a method for determining the brittle points of rubber materials in cold air. A method to determine resistance to cracking by flexing specimens in cold air was developed by Martin[3]. However, the latter test is not entirely satisfactory, as the specimens are bent in a rather large loop instead of being subjected to a blow of definite impact combined with bending. Such a test may qualify a material for a lower temperature than it can withstand in some types of service. To simulate the severest type of service conditions, it is believed desirable to determine brittle point by subjecting specimens to the combination of a blow of definite impact and bending through 90° in cold air.

Additional papers recently presented at the Fall Meeting of the Rubber Division of the American Chemical Society[4,5,6], dealt further with the behavior of rubbers and synthetic rubbers at low temperatures. Liska[5] presented interesting data which indicates that brittleness and stiffness are not necessarily correlated; thus, two samples may have essentially the same brittleness and one of them be so stiff as to be unsuitable for use, whereas the other sample may show a much lesser degree of stiffness.

One of the authors recently developed a method of measuring the force required to deflect which has been in use in several of the Navy laboratories for several months. The dyne tensiometer method[4] is a modification of this method. It is believed that, to make a complete evaluation of the characteristics of the rubber or rubberlike materials at low temperatures, it is desirable to measure brittleness as well as stiffness.

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APPARATUS

The low-temperature cabinet used in the tests is shown in Figure 1. The cabinet has wood exterior and interior walls, separated by 6 inches of glass-wool batting. The lid contains a triple-layer glass window 9 inches square for observation of the test, and a fan for circulation of cold air through the dry-ice

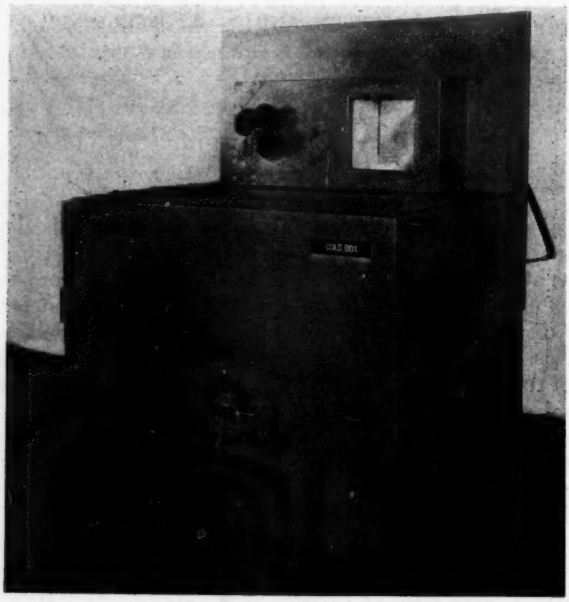

FIG. 1.—Low temperature cabinet.

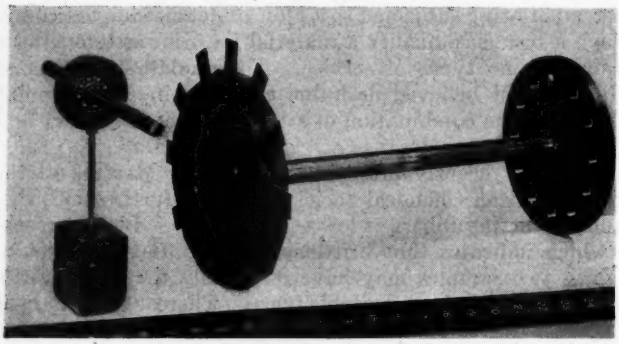

FIG. 2.—Parts of brittle point apparatus.

compartment and communicating working chamber. The working chamber is also provided with a fan for continuous circulation of air, and is illuminated by a 50-watt lamp.

A manually-controlled damper for regulating the amount of air passed over the dry ice is located in the partition between the two compartments. During

the test, any selected low temperature down to −95° F can be held within the limits of ±½° F by manual control, or ±2° F by means of a thermoregulator. Temperature in the working chamber was measured by means of a copper-constantan thermocouple and a potentiometer type pyrometer.

The essential parts of the brittle-point apparatus are a specimen jig designed to accommodate 12 test specimens, and a pendulum hammer for striking the specimens. These parts are shown in Figure 2.

The specimen jig is secured to a shaft that is connected to a control plate mounted outside the cabinet. The specimens are clamped between an outer Bakelite and an inner steel plate, and are insulated from the steel plate by a single thickness of cardboard. The Bakelite plate is constructed so that the twelve flats on the periphery are 0.25 inch below the corresponding flats on the

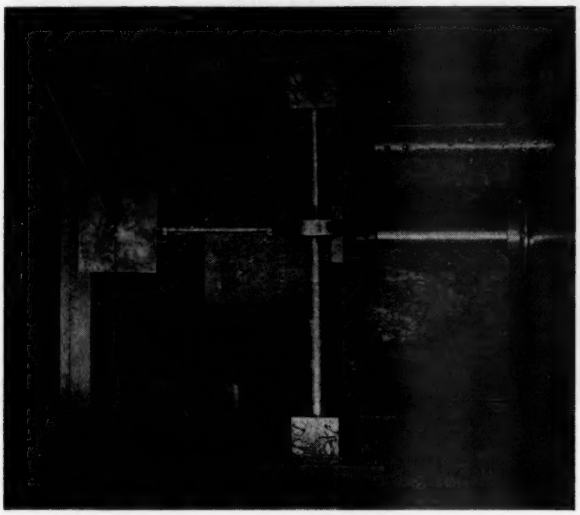

FIG. 3.—Jig mounted in cold box.

steel plate, thereby exposing one side of the specimen over a length 0.25 inch longer than on the other side. The maximum distance between flats is 8.2 and 8.7 inches for the Bakelite and the steel plates, respectively. The control plate is stamped with numbers to correspond with the position of specimens secured in the jig. The specimen to be tested is brought into position by revolving the shaft. A pin lug fitting into the control plate secures the shaft in the selected position.

A pendulum hammer made of steel is supported by a shaft mounted directly above the specimen jig. To assure free swing of the hammer, it is attached to the shaft through a collar containing a dry ball-bearing. The hammer is 3 inches long, 3 inches high and 2 inches wide, and has a leading edge rounded to a radius of 1 inch. The radius of swing of the hammer is 8.5 inches, and there is a clearance adjusted to 0.25 inch between the lower surface of the hammer and the flats on the steel plate of the specimen jig. A cord, attached to the hammer and passing through a hole in the lid of the cabinet, is the means by which the hammer is raised to level position for striking the specimen.

METHOD OF TEST

Specimens 1 × 2.5 inches were died from test sheets 0.080 ± 0.005 inch thick. All specimens were buffed on both sides, as it was found in preliminary tests that unbuffed specimens did not always break off clean at the critical temperature of fracture. A total of twelve specimens, consisting of two speci-

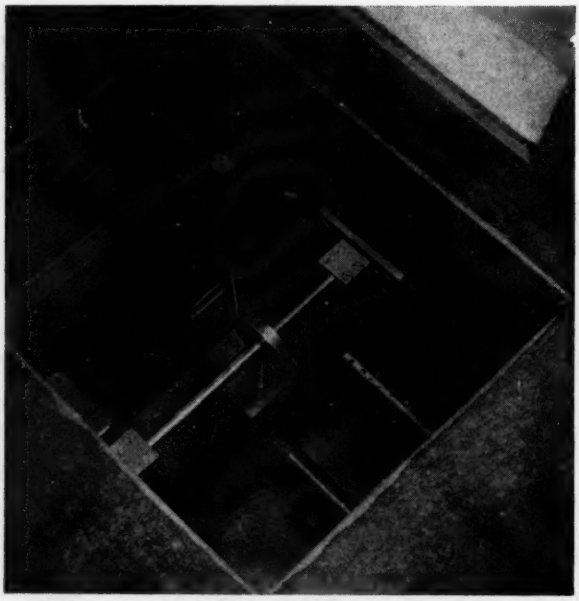

FIG. 4.—Position at instant of impact.

TABLE I

Type of rubber	Brittle point (degrees F): Temperature limit before failure of specimen (° F)	Brittle point (degrees F): Temperature at Failure (° F)
Deresinated guayule	−72, −72	−73, −73
Buton-S	−62, −62	−63, −63
Butaprene-NMX	+ 7, + 6	+ 5, + 5
Butaprene-NM	−30, −31, −31	−32, −32, −32
Butaprene-NM	−58, −59	−60, −60
Butaprene-NX	0, − 1, − 1	− 2, − 2, − 2
Chemigum-I	−15, −15	−16, −16
Chemigum-I	−53, −54, −54	−55, −55, −55
Chemigum-X	+30, +29, +29	+28, +28, +28
Hycar-OR-15	−32, −33, −33	−34, −34, −34
Hycar-OR-25	−18, −19, −19	−20, −20, −20
German Perbunan	−32, −33, −33	−34, −34, −34
Stanco Perbunan-26	−30, −31, −31	−32, −32, −32
Stanco Perbunan-26	−64, −65, −65	−66, −66, −66
Thiokol-RD	−10, −12	−13, −13
Neoprene-E	−32, −33, −33	−34, −34, −34
Neoprene-FR	−48, −49, −49	−50, −50, −50
Neoprene-FR	−68, −68	−69, −69
Neoprene-GN	−32, −33, −33	−34, −34, −34
Thiokol-F	−18, −19, −19	−20, −20, −20
Thiokol-FA	−30, −31, −31	−32, −32, −32

TABLE II

	Deresinated guayule	(Buton-S)	Butaprene-NMX	Butaprene-NM	Butaprene-NM	Butaprene-NX	Chemigum-I	Chemigum-I	Chemigum-X	Hycar-OR-15	Hycar-OR-25	German Perbunan	Stanco Perbunan-26	Stanco Perbunan-26	Thiokol-RD	Neoprene-E	Neoprene-FR	Neoprene-FR	Neoprene-GN	Thiokol-F	Thiokol-FA
Deresinated guayule	100.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Buton-S	...	100.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Butaprene-NMX	...	...	100.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Butaprene-NM	...	...	...	100.0	100.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Butaprene-NX	...	...	...	...	...	100.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Chemigum-I	...	...	...	...	...	...	100.0	100.0	...	...	...	...	...	...	...	...	...	...	...	...	...
Chemigum-X	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...	...	...	...	...	...	...	...
Hycar-OR-15	...	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...	...	...	...	...	...	...
Hycar-OR-25	...	...	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...	...	...	...	...	...
German Perbunan	...	...	...	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...	...	...	...	...
Stanco Perbunan-26	...	...	...	...	...	...	...	...	...	...	...	...	100.0	100.0	...	...	...	...	...	...	...
Thiokol-RD	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...	...
Neoprene-E	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...
Neoprene-FR	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100.0	100.0	...	...	...
Neoprene-GN	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100.0	...	...
Thiokol-F	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100.0	...
Thiokol-FA	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100.0
Pelletex (carbon black)	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	10.0	...	...	5.0	10.0	10.0
Stearic acid	2.0	...	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	1.0	1.0	0.5	0.5	0.5
Neozone-A (phenyl-α-naphthylamine)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0	2.0	...	...
Altax (benzothiazyl disulfide)	0.8	...	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	...	...	...	...	0.35	0.30
Dibutyl sebacate	...	...	...	...	10.0	...	...	10.0	...	10.0	...	...	...	10.0	10.0	...	...	10.0	...	...	...
Dibutyl phthalate	...	...	...	...	10.0	...	...	10.0	...	10.0	...	...	...	10.0	10.0	...	...	10.0	...	...	...
Diisobutyl adipate	...	...	...	...	10.0	...	...	10.0	...	10.0	...	...	...	10.0	10.0	...	...	10.0	...	...	...
Litharge	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10.0	10.0	...	...	...
Magnesia	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10.0	...	...	4.0	...	...
Wood rosin	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	5.0	...	...	...	...	...
Diphenylguanidine	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.10	0.10
Zinc dimethyldithiocarbamate	0.1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Tetramethylthiuram monosulfide	...	0.5	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Micronized sulfur	...	...	...	...	1.75	...	...	1.75	...	1.75	...	...	...	1.75	1.75	...	...	...	...	...	...
Sulfur	2.5	2.0	1.75	1.75	...	1.75	1.75	...	1.75	...	1.75	1.75	1.75	...	...	1.0	1.0	1.0	...	...	...

mens each of six different materials, were arranged radially between the plates of the jig, and clamped in position so that each specimen projected 1.25 inch beyond the flat surface of the steel plate. The jig was mounted in the cold box, as shown in Figure 3. The approximate brittle point of each material was determined by subjecting the specimens to one or two blows of the pendulum hammer at temperatures decreased from room temperature in steps of 5° F. However, the specimens were conditioned for 10 minutes at each temperature before testing.

To determine the brittle point of each material more exactly, the tests were repeated in steps of 1° F decrease in temperature in the brittleness range of the material. The highest temperature at which the specimen broke after being conditioned for 10 minutes at that temperature was taken as the brittle point of the material. The apparatus before and at the instant of impact of the pendulum hammer is shown in Figures 3 and 4, respectively.

MATERIALS TESTED AND RESULTS

Stocks prepared from the following rubbers were tested:
Natural: deresinated guayule
Buna-S type: Buton-S
Buna-N type: Butaprene-NMX, Butaprene-NM, Butaprene-NX, Chemigum-I, Chemigum-X, Hycar-OR-15, Hycar-OR-25, German Perbunan, Stanco Perbunan, Thiokol-RD
Chloroprene type: Neoprene-E, Neoprene-FR, Neoprene-GN
Organic polysulfides: Thiokol-F, Thiokol-FA
The detail formulations are given in Table II.

The results are given in Table I. In most cases the check tests were made on separate days.

CONCLUSION

The method described herein for determining brittle point is relatively simple, and the results are indicative of the ability of the material to withstand impact combined with bending. It is believed that this combination will more correctly evaluate brittle point than a bent loop test or other moderate flexing tests. If the material is exposed to low ambient air temperatures in service, then tests to determine brittle point should be made in cold air and not in an immersion bath. Appreciable differences in brittle point are obtained by judicious modifications in compounding ingredients of Buna-N and chloroprene synthetic rubbers.

ACKNOWLEDGMENT

The authors wish to thank H. Nestlen for his advice and O. Retkoff, who performed a large part of the testing. The authors are also indebted to Ross E. Morris, of the Rubber Laboratory, Navy Yard, Mare Island, California, who furnished the rubber stocks.

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REPORT OF THE CRUDE RUBBER COMMITTEE PRESENTED TO THE DIVISION OF RUBBER CHEMISTRY, APRIL 26, 1944

CORRECTION

The most recent Report of the Crude Rubber Committee, published on pages 529–532 of the April 1944 issue of RUBBER CHEMISTRY AND TECHNOLOGY, itemizes certain types of "scrap" rubber incorrectly as *Hevea* rubber, whereas they should be designated as *Castilloa*.

This error occurs in the table on page 530, in which the scrap from Ecuador, Guatemala, Honduras, Costa Rica, Panama, Colombia and Nicaragua should be shown to be from *Castilloa* instead of from *Hevea* as now designated in the third column.

PHYSICAL METHODS OF ANALYSIS OF SYNTHETIC AND NATURAL RUBBER

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CORRECTION

In the article of the title above, on pages 253–266 of the April 1944 issue of RUBBER CHEMISTRY AND TECHNOLOGY, an error appeared in the article as originally published in *Industrial and Engineering Chemistry*. This error appears also in the transcribed version in RUBBER CHEMISTRY AND TECHNOLOGY.

On page 264, the paragraph following Table III should read as follows:

Method II (adopted for solution of rubber and separation of pigments).—Sheet the sample to a thickness of approximately 0.0375 cm. (0.015 inch) on a tight cold 15 × 30 cm. (6 × 12 inch) laboratory mill.